TEMPERATURE DEPENDENCE OF EXCESS THERMODYNAMIC PROPERTIES OF ETHANOL-HYDROCARBON SYSTEMS

A THESIS

Presented to

The Faculty of the Graduate Division

by

Stephen Chi Ping Hwa

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School

of Chemical Engineering

Georgia Institute of Technology

July, 1963

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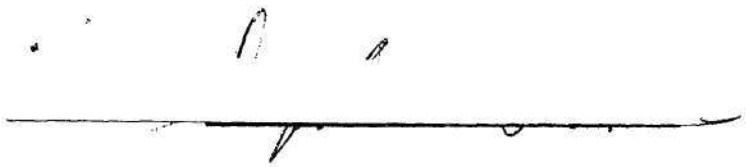

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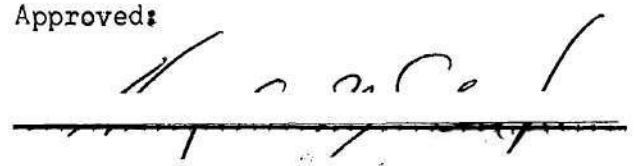

Date approved by Chairman: Sept 18, 1963

DEDICATION

To my father and mother

ACKNOWLEDGMENTS

The author wishes to express sincere gratitude to his thesis adviser, Dr. W. T. Ziegler, for his unstinting effort to introduce the author to the methods of experimentation and the proper attitude toward research. The completion of this thesis owes much to his advice and guidance and also to his patience in improving the English of the manuscript.

The author wishes to acknowledge the help of Mr. B. S. Kirk, who gave many valuable suggestions, particularly in the designing of the temperature control system, and also the aid of Mr. J. C. Mullins, who has kindly helped him to learn the use of the Burroughs 220 digital computer. Appreciation is due to Dr. W. M. Newton and Dr. H. A. McGee, Jr., for the reading of this manuscript. Appreciation is also due to the Engineering Experiment Station and Chemical Engineering Department for financial support of part of the work described herein, and to the Rich Electronic Computer Center for the use of the computing facilities.

In addition, the author is grateful to Dr. I. Brown of Chemical Research Laboratory, Australia, and Dr. H. C. Van Ness of Rensselaer Polytechnic Institute for making available to him their unpublished works.

Finally, the author wishes to express his appreciation to his wife, Theresa, whose love, encouragement and actual help has made this work possible.

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SUMMARY

The objectives of this research were to study the method for obtaining excess thermodynamic properties, G^E, H^E, S^E, and C_p^E, over a wide temperature range, to determine experimentally the temperature dependence of excess thermodynamic properties of two systems (ethanol-methylcyclohexane and ethanol-toluene) which have been otherwise well studied near room temperature, and to test the current theory of associated solutions with these properties.

It was decided to measure the excess heat capacity of these two systems over a wide temperature range; these data could then be used to derive other excess properties in that temperature range. The heat capacity measurements were carried out in a precision adiabatic-shield type, high-vacuum calorimeter. This calorimeter was also used to determine the purity and the nominal melting point of the purified toluene, methylcyclohexane and ethanol samples.

The heat capacity measurements were made on the three pure components, toluene, methylcyclohexane and ethanol, in the temperature range from 35°C. to -95°C., to -100°C., and to -110°C., respectively. For the ethanol-methylcyclohexane system, measurements were made over the temperature range of 35°C. to -65°C. at the following compositions: 0.0742, 0.1979, 0.3456, 0.5324 and,0.8004 mole fraction of ethanol. For the ethanol-toluene system, measurements were made over the temperature range of 35°C. to -95°C. at the following compositions: 0.0630, 0.0969,

0.1841, 0.2748, 0.4505, 0.6439, and 0.8026 mole fraction of ethanol. The excess heat capacity was calculated using the heat capacity data of the mixture and the pure components. The heat capacity of toluene and methylcyclohexane has been accurately measured before[33,34]. The heat capacity of these two liquids measured in this work agrees within the accuracy uncertainty of the earlier values. The accuracy uncertainty of the heat capacity measurements of this work is estimated to be within 0.2 per cent, and the accuracy uncertainty in the excess heat capacity data is probably within 0.06 cal./gm.mole °C.

The heat of mixing and vapor liquid equilibria of these two systems have been measured at 35°C.[36,37,38,39,40]. These data and the excess heat capacity data were used to derive G^E, H^E, and S^E of these two systems. The excess properties were derived at five degree intervals from 35°C. to -85°C. for the ethanol-methylcyclohexane system, and from 35°C. to -105°C. for the ethanol-toluene system. The free energy of mixing, G^M, of these two systems was also calculated at the same temperature intervals. The activity coefficients were calculated at 0°C., -25°C., -50°C., and -75°C. for the ethanol-methylcyclohexane system, and at 0°C., -25°C., -50°C., -75°C., and -100°C. for the ethanol-toluene system.

The temperature dependence of the excess thermodynamic properties of the ethanol-methylcyclohexane system in the temperature range studied can be briefly described as follows: The maximum of the excess enthalpy decreases from about 160 cal./gm.mole at 35°C. to about 65

cal./gm.mole at -40°C. and remains constant below this temperature. The maximum point in the excess enthalpy vs. composition curve situated in the dilute ethanol composition range at high temperatures shifts to the ethanol rich composition range at low temperatures. The minimum of excess entropy decreases from about -0.58 e. u. at 35°C. to -0.90 e. u. at -40°C. with the minimum shifted to the dilute ethanol region at low temperature. Although the excess free energy decreases with lowering of temperature, the change with temperature is slow and therefore the system becomes increasingly nonideal, as shown by the increase of the activity coefficients with decreasing of temperature. Eventually, the nonideality leads to the phase separation at about -78°C. as shown from the plot of the extrapolated free energy of mixing and also shown by qualitative cloud point tests.

The temperature dependence of these properties of the ethanol-toluene system are different from those of the previous system in the following way: The maximum of the excess enthalpy decreases more rapidly than the previous system from a value of about 230 cal./gm. mole at 35°C. to about 30 cal./gm.mole at -50°C. with the maximum located in the very dilute ethanol region. The excess enthalpy values are slightly negative in the very concentrated ethanol region at -50°C., and become almost negative over the entire concentration range at -95°C. with the minimum value at about -20 cal./gm.mole. The excess entropy, though considerably larger than the previous system at 35°C., is slightly more negative than for the previous system below -40°C. The excess free

energy decreases more rapidly with lowering of temperature than for the previous system. The system becomes less nonideal in the low temperature range, as shown by the activity coefficients approaching unity.

The behavior of the excess thermodynamic properties of ethanol-methylcyclohexane system near room temperature has been successfully interpreted by the model which assumes that hydrogen bonding between ethanol molecules leads to the formation of linear polymeric ethanol species in the liquid and that the concentration of the solution affects the equilibrium distribution of the various species, dimer, trimer, etc.[24]. In order that the same model could be used to describe qualitatively the temperature dependence of the excess properties, a temperature dependence of the model, which will be described later, was suggested.

A similar model, which assumes, in addition to the hydrogen bonding, an association between the aromatic molecule and the ethanol species and that such association affects the equilibrium distribution of the various ethanol species, has been used to interpret the behavior of the excess thermodynamic properties of ethanol-toluene system near room temperature[24]. However, this model cannot consistently describe qualitatively the derived properties at low temperature. An additional interaction between the toluene molecule and ethanol species which does not affect the equilibrium distribution of the ethanol species has been postulated. The inclusion of this additional interaction has made possible a qualitative explanation of the temperature dependence of the excess enthalpy and entropy of the ethanol-toluene system.

The quantitative treatment which is based essentially on the model described above for the ethanol-methylcyclohexane system has been used to correlate the excess properties with composition of this system and the related systems by Kretschmer and Wiebe[21] using the excess properties measured near room temperature. One of their simplifying assumptions is that the equilibrium constants for the association reaction between any two ethanol species have the same value. A similar theoretical treatment (with the main difference that two equilibrium constants were used, one for the dimerization reaction, the other for the association reactions other than dimerization) has been employed in this work to correlate the derived excess free energy data and excess enthalpy data of the ethanol-methylcyclohexane system at several temperatures ranging from 35°C. to -75°C. It was found that the two-constant treatment could correlate the excess free energy and excess enthalpy with composition to within the uncertainty of the derived data; while the one-constant treatment used by Kretschmer and Wiebe could not correlate the excess free energy data at low temperatures and the excess enthalpy data to within the uncertainty of the derived data.

The parameters used in this treatment are: the equilibrium constant of the dimerization reaction and the equilibrium constant for other association reaction; the enthalpy of formation of the hydrogen bond; and the heat of mixing due to nonideal mixing between the ethanol species and the methylcyclohexane molecules. These parameters were

estimated for the ethanol-methylcyclohexane system at 35°C., 0°C, -25°C., -50°C., and -75°C.

The above quantitative treatment considers that the excess enthalpy of the mixture consists of two parts, one arising from the breaking of hydrogen bonds in the forming of a solution and the other resulting from the nonideal mixing between the ethanol species and the methylcyclohexane molecules. The correlation showed the temperature dependence of the model to be, briefly, as follows. The contribution to the excess enthalpy from the breaking of hydrogen bonds decreased with lowering of temperature and became negligible below -40°C.; this is due to the decrease of both the number of hydrogen bonds being broken and the enthalpy of breaking the bond. The nonideal mixing between the ethanol species and the methylcyclohexane molecules contributes a maximum of about 60 cal./gm.mole to the excess enthalpy; this value is essentially temperature independent. This is consistent with the previously suggested temperature dependence of the model.

The fact that two different processes: (1) qualitative analysis of the temperature dependence of the excess thermodynamic properties, and (2) quantitative correlation of the isothermal excess thermodynamic properties with composition lead to the same result is an indication that the model used is consistent with the actual properties of the solution.

LIST OF SYMBOLS

The symbols used in the text, if not otherwise stated, denote the following terms:

A	cryoscopic constants
B	per cent melted
b	a constant
C	concentration or molal heat capacity
°C.	degree Celsius (centigrade)
D	volume fraction
e	base of natural logarithms
G	Gibbs free energy
$\bar{G}$	partial molal Gibbs free energy
H	enthalpy
K	equilibrium constant
°K.	degree Kelvin
ln	natural logarithm
n	number of moles
n_D^{20}	index of refraction for sodium light at 20°C.
P	pressure
R	gas constant
S	entropy
T	absolute temperature in °K.
t	temperature in °C.
V	molal volume

x	mole fraction
y,z	variables

GREEK ALPHABET

γ	activity coefficient
μ	Chemical potential
$\sum$	summation
θ	coordination number for the lattice
ρ	symmetry number

SUBSCRIPTS

a	of alcohol, stoichiometric
c	of concentration
f	of fusion
mp	of melting point
h	of hydrocarbon, stoichiometric
P	at constant pressure
T	at constant temperature
x	at constant composition
1,2, ..., i,...j, ...	of species consisting of 1,2, ..., i,...j, ... units of alcohol molecules

SUPERSCRIPTS

E	excess property
M	property of mixing
R	property of reaction
S	property of solution or mixture
o	property of pure component
oo	property of pure species at an oriented state

CHAPTER I

INTRODUCTION

Recent progress in the theories of nonelectrolyte solutions has made it possible to explain satisfactorily the behavior of various solutions qualitatively. For only a few particular classes of solutions: regular solutions (1); associated solutions (2); congruent mixtures of n-alkanes (3), for example, has the theory been successfully used to correlate experimental data. Such successful correlation usually involves the use of adjustable parameters. It is clear that the theories in this field are not entirely satisfactory for the practical use of quantitatively predicting properties of a solution. An improvement of the theories of solutions is very much needed so that these theories can be of practical use.

In recent years much effort has been given to the experimental studies of solutions. However, these efforts have been distributed to so many binary systems that the properties of each system are yet incompletely known. For example, the excess thermodynamic properties of a solution are usually only known at one temperature or for a short temperature range, insufficient to reveal the temperature dependence of the properties. One can hardly expect to formulate a theory that will predict quantitatively the properties of a certain system, if the behavior of this system and the related systems are not satisfactorily known.

A concerted study of a few selected systems by measurements of spectroscopy, transport properties, and excess thermodynamic properties over a wide temperature range may provide a better understanding of these systems and perhaps lead to a better theory.

The primary objectives of this work were: to study the method for obtaining excess thermodynamic properties over a wide temperature range, to determine experimentally the temperature dependence of excess thermodynamic properties of two systems (ethanol-methylcyclohexane and ethanol-toluene) which have been otherwise well studied, and to test the current theory of associated solutions with these properties.

The four excess thermodynamic properties: G^E, H^E, S^E, and C_p^E,[4] are related to each other by thermodynamic relations as shown in Chapter V. If one of the properties is measured over a certain temperature range, these data can be used to calculate other excess properties in this range. Therefore, the necessary experimental work to study temperature dependence of the four excess properties is reduced to the measurement of any one of the properties. The usual apparatus for measuring vapor-liquid equilibria, from which excess free energy can be calculated, is very limited in operating temperature range[5]. Also, the computation from vapor-liquid data, even with the best data, leaves the finer details uncertain and can give no reliable information on the temperature dependence of the heat of mixing[6]. Heat of mixing and excess heat capacity or, more precisely, heat capacity of the solution can be measured over a wide temperature range. Heat capacity measurement was selected in this work for its experimental simplicity and the availability of equipment.

Measurements of heat capacity of binary solutions made in the last decade were briefly reviewed by Rowlinson[5] in 1959. There are few works published thereafter[7,8]. The early work of Williams and Daniels[9] covered five systems, but their measurements have low accuracy. Most published measurements have covered only a short temperature range, with few studies covering a range of as much as fifty degrees centigrade. Unfortunately, many of the published measurements are of low accuracy. As a result, even the sign of the computed excess heat capacity is in doubt. For example, the heat capacity measurements of Staveley, et al.,[10] were stated to have an accuracy of ± 1 per cent. One of the systems, benzene and ethylene dichloride, measured by them between 20°C. and 70°C., has a maximum excess heat capacity of less than ± 0.4 cal./gm.mole °C.; while the measured heat capacity of the mixtures was between 30 to 35 cal./gm.mole °C. Therefore, the magnitude of the excess heat capacity of this system is close to the uncertainty of the measurement. Since excess heat capacity, even for the very nonideal solution, is usually less than 15 per cent of the measured heat capacity of the solution, the accuracy of the measurement is the primary limiting factor for obtaining meaningful values of the excess heat capacity.

Two systems, ethanol-methylcyclohexane and ethanol-toluene, were selected for study in this work. The excess free energy and heat of mixing of both systems have been well studied near room temperature. These data can be used as initial values for deriving excess properties at other temperatures.

The binary solutions of alcohol and nonpolar solvent have attracted the interests of both theoretical and experimental workers. One of the reasons for such interest is that a major part of the nonideal behavior of these solutions can be attributed to hydrogen bonding. These solutions are generally called associated solutions[2].

Tompa[11] and Barker[12,13] have applied to the liquid solutions a quasilattice model which postulates different types of contact points on the molecule or different specific interactions between molecules. Barker[12] and Goates, et al.,[14] have successfully used this theory to correlate properties of alcohol-nonpolar solvent (associated) solutions.

Dolezalck[15] correlated the nonideal behavior of solutions by assuming that the interactions caused the molecules to form associated complexes as in chemical reactions. For the alcohol molecule, such association could lead to polymeric species. This continuous association concept was first used by Lassettre[16] and then improved by Tobolsky and Blatz[17], Flory[18], Relich and Kister[19], and Scatchard[20]. Redlich and Kister[19], Kretschmer and Wiebe[21], and Papousek, et al.,[22] have successfully employed the concept of continuous association to correlate the properties of solutions containing alcohols and nonpolar solvents. This treatment will be referred to hereafter as the "associated theory of solution."

None of these theories has been applied to excess properties of solutions over a wide temperature range, primarily due to lack of data. An objective of this study was to determine whether the associated theory

of solution was able to correlate consistently the excess properties of a solution (ethanol-methylcyclohexane) over a wide temperature range, as well as how the various interactions assumed in the associated theory changed with temperature.

Among the group of alcohol-hydrocarbon solutions, the systems involving paraffins always show a smaller solubility and a higher upper critical solution temperature than those systems containing unsaturated hydrocarbons of similar paraffinic structure. This appears to be a general characteristic of the solutions of hydrocarbons and polar substance. For example, Prausnitz[23] found that ethylene gas had a higher solubility than ethane in polar liquids at the same temperature and pressure; he has attributed this behavior to the interaction between the π-electrons of the double bond and the acidic polar components. The analysis of the thermodynamic data and spectroscopic data of alcohol-aromatic solutions has indicated the presence of an interaction between the π-electron and the proton of the hydroxyl group[24,25].

In the ethanol-methylcyclohexane system, the presence of hydrogen bonding is anticipated; while in the ethanol-toluene system, the additional interaction between the π-electrons of the aromatic ring and the hydroxyl group should be expected. These two systems represent the two different classes of alcohol-hydrocarbon solutions. It was hoped that the study of these two systems over a wide temperature range might reveal the general characteristics of such alcohol-hydrocarbon solutions.

CHAPTER II

EXPERIMENTAL APPARATUS AND PROCEDURE

Description of Apparatus

The apparatus used to carry out the heat capacity measurements is a precision adiabatic-shield type high-vacuum calorimeter suitable for measurements from 15°K. to 350°K. In general design it is similar to the one described by Scott, et al.[26]. The calorimeter had been used previously and is described elsewhere[27,28]. The limited description of the apparatus given below follows closely that given elsewhere[28]. For purposes of the present experiments, certain changes, described below, have been incorporated.

A schematic diagram of the apparatus is shown in Figure 1. Briefly the apparatus consists of a copper calorimeter can, C, (in which the sample of the liquid to be studied is sealed) surrounded by a vacuum jacket, V, which is immersed in a suitable bath, B.

The vacuum jacket can be evacuated through the line, L, or helium gas can be admitted to this space when it is desired to cool the calorimeter can to the temperature of the bath. The calorimeter can is surrounded by a lightweight copper shield, S, the temperature of which can be adjusted to the same temperature as the calorimeter can to within about 0.01°C., thus eliminating radiation transfer between the calorimeter can and its surroundings. The temperature difference between calotimeter can and adiabatic shield is sensed by four three-junction

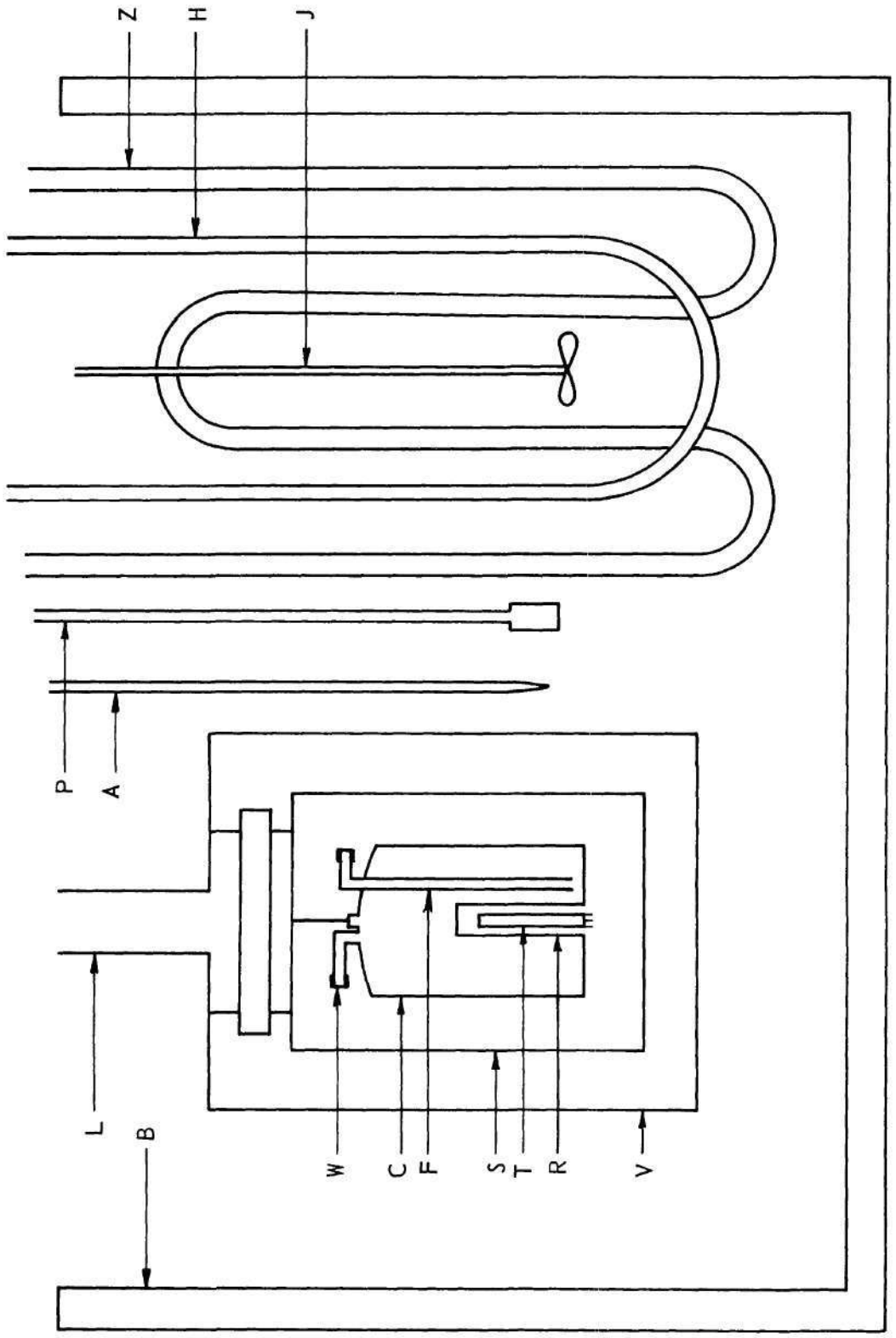

Figure 1. Schematic Diagram of Calorimeter.

difference-thermocouples. Manual control of the temperature difference is achieved by regulation of the power supplied to three electrical resistance heaters wound on the top, sides, and bottom of the shield. In earlier heat capacity measurements[27,28] several different constant temperature baths (for example, ice-water, solid carbon dioxide-alcohol) were used outside the vacuum jacket. Each bath was used for measurements over a certain temperature range. Thus, some measurements were carried out with the temperature of the vacuum jacket much lower than the temperature of the shield and the can. Such an arrangement has the following disadvantages:

1. It is difficult to attain a desired starting temperature, if this temperature is not the temperature of the bath.

2. One person must devote his entire attention to the control of the shield temperature.

3. A correction term must be added to the heat capacity data measured in the high temperature range, since the calorimeter can was observed to have a small cooling drift in temperature even though the difference-thermocouples indicated negligible temperature difference between the shield and the can. (Presumably, the high radiation heat loss from the shield caused uneven temperature distribution on the shield.)

In order to eliminate these deficiencies, a bath was constructed as shown in Figure 1. The bath container, B, is a Pyrex jar, 8-1/4 inches in diameter and 18 inches deep, placed in a metal container with about a one inch gap between the jar and the metal container, which was

filled with polyurethane foam. The cooling coil, Z, is connected to a liquid nitrogen Dewar vessel (not shown in Figure 1). When the Dewar vessel is pressurized, liquid nitrogen flows into the cooling coil and serves as a refrigerant for the bath. The temperature-sensing probe, P, consists of three different thermistors, each coated with silicone rubber, imbedded in the brass probe with Wood's metal. Each thermistor, suitable for a certain temperature range, can be connected as an arm of a Wheatstone bridge. When the bridge is balanced for a certain bath temperature, the warming up of the bath changes the resistance of the thermistor and unbalances the bridge. The signal from the bridge actuates a solenoid valve which connects a pressurized nitrogen gas line to the liquid nitrogen Dewar vessel, thereby transferring liquid nitrogen to the cooling coil. The probe and the cooling coil together constitute a temperature control system capable of maintaining the bath at a constant temperature to ± 0.2°C. at any preset temperature between -130°C. and room temperature. The stirrer, J, is a variable speed type, with an induction type motor suitable for operating in an inflammable atmosphere. The heater, H, is a 500 watt flexible immersion type connected to a Variac transformer. By adjusting the Variac, the bath temperature can be easily controlled so as to follow closely the temperature of the adiabatic shield and thus minimizing the radiation heat loss from the shield. The thermocouple, A, made of copper wire (B. and S. No. 34 gauge, single cotton enameled wire, Anaconda Company) and of constantan wire (B. and S. No. 32 gauge, double nylon enameled wire, Advance brand,

Driver-Harris Company) is inserted in a glass tube filled with 2-methylpentane. A Rubicon portable precision potentiometer (model 2745, Minneapolis-Honeywell Company) was used with the thermocouple to measure the temperature of the bath. The thermocouples used were made of wires taken from the same spools which had been previously calibrated[28].

Three different bath liquids were used: water was used above 0°C.; ethanol was used in the range -65°C. to 0°C.; and 2-methylpentane was used in the range -130°C. to -65°C. The liquids and their working range were selected because of the suitabilities of their viscosity, vapor pressure, and flash point.

Some change was made on the calorimeter can, C, used in previous measurements[27,28]. The original filling port was sealed and a filling tube, F, and a withdrawal tube, W, were installed at the top of the can. Both tubes are thin wall Monel tubing (1/8 inch O. D., 3/32 inch I. D.) soldered to specially machined elbows which were soldered to the top of the can. The liquid inside the calorimeter can may be drained completely by inverting the can. Two brass caps, each weighing about 0.2 gram, were used to seal these tubes by soldering. Since the Monel tubing is a poor conductor, the heat required for soldering is prevented from evaporating a significant amount of liquid in the can.

The primary temperature measurements were made with a Leeds and Northrup capsule-type precision platinum resistance thermometer, T, (Leeds and Northrup No. 1048215) which had been calibrated by the National Bureau of Standards on the International Temperature Scale down to the

normal boiling point of oxygen (-182.970°C.). All measurements with this thermometer were made with a Leeds and Northrup Mueller G-2 resistance bridge which permitted the temperature of the calorimeter can to be determined to about 0.001°C. (0.0001 ohm).

Energy measurements were made by accurately measuring the current through and potential across the calorimeter heater, R, during the heating interval by means of a Leeds and Northrup 100,000-microvolt White double potentiometer. The standard resistors and standard cells used had been calibrated by the National Bureau of Standards. The heating time, which was controlled manually, was determined with a 110-volt, 60-cycle type S-10 electric timer manufactured by The Standard Electric Timer Company, Springfield, Massachusetts. Previous analysis[27] of the accuracy of this timer and manual operation of the switches indicated that the time of the heating interval could be determined to ± 0.1 sec.

Experimental Procedure

Preparation of Sample

A desired amount of purified ethanol and hydrocarbon was transferred to a specially constructed weighing bottle which weighed 30 gm. when empty, and had a marked volume of 170 ml. The weight of each material added to the weighing bottle was measured with an analytical balance accurate to 0.001 gm. The sample was thoroughly mixed in the weighing bottle and then transferred to the calorimeter can. The empty can, which weighs 193.5 gm. and has a volume of 160 ml., was filled to about 10 ml. of capacity. All the transfer of liquids was carried out by

exerting dry nitrogen gas pressure on the liquid forcing the liquid to flow out through a submerged glass tube which was connected to the receiving end by a tightly fitting Teflon tube. The can was then sealed with 50-50 lead-tin solder by soldering the two brass caps to the filling and withdrawal tubes. The weight of liquid in the can was obtained by noting the difference in weight of the weighing bottle before and after transfer, and was also checked by weighing the empty and the filled calorimeter can on a rough balance which was accurate to ± 0.02 gm. The two results always agreed to within 0.06 gm. for a total sample weight of about 120 gm., indicating that the amount of liquid lost during transfer and soldering was negligible. During repeated sealing and removing of the two caps, the amount of solder on the tubes was found to vary within 0.02 gm. No correction was made in the heat capacity calculation for this small variation.

Heat Capacity Measurements

After the calorimeter can was sealed inside the vacuum case, the whole system was tested for vacuum tightness and electrical grounding. Helium gas was then admitted to the vacuum jacket and the calorimeter and its contents were cooled to the temperature of the bath which was maintained at the desired temperature by the temperature control system. The calorimeter system was then evacuated to about 1×10^{-6} mm. Hg. pressure and the system was ready for making measurements.

Measurement of heat capacity was accomplished by noting the energy required to heat the can and its content through a known temperature interval. Once the can was heated above the initial bath

temperature, the temperature control system of the bath was shut off and the heater unit of the bath was used instead. By adjusting the Variac of the heater unit, the temperature of the bath could be easily maintained to two degrees or less below the temperature of the can even during the heating period of the calorimeter. In the mean time, the adiabatic shield was adjusted to the same temperature as the can. With this arrangement, the environment of the calorimeter can was so close to adiabatic condition that the drift of the temperature of the can, as shown by the Mueller bridge, was usually less than 0.002°C./hr. A heat capacity measurement usually took a total of 30 minutes. Therefore, no correction was made in the heat capacity calculation for this slow drift in temperature.

An Edison battery was used as the power source for the calorimeter heater. The variation of the input power produced by a slight drift in the battery voltage and the change in the resistance of the heater wire was found to be less than 0.04 per cent for each measurement. Therefore the power input to the heater was considered to be constant and the value obtained in the middle of the heating period was used for the heat capacity calculation.

Briefly, the measurements were carried out as follows:

1. The initial resistance of the resistance thermometer was recorded.

2. The heater in the calorimeter can was switched on and the voltage across the one ohm standard and the voltage across the heater, or more precisely, across the volt box, were recorded.

3. The heater was switched off; the heating time and the final resistance of the thermometer were recorded after the temperature of the can was steady. It usually took less than ten minutes for the temperature of the can to become constant after the heater had been shut off.

Whenever circumstances permitted, the measurement was carried out continuously, i.e., the final temperature of one measurement was used as the initial temperature for the next measurement. The temperature interval covered by each measurement varied from three to five degree centigrade. The heating period varied from 600 to 1200 seconds. The heat capacity measurements and control of the temperature of the bath and the shield could easily be accomplished by one person.

CHAPTER III

PURIFICATION AND CHARACTERIZATION OF MATERIALS

Source and Purification

Toluene and methylcyclohexane were obtained from the Phillips Petroleum Company. Both materials were stated to be 99 mole per cent minimum purity by the supplier. Absolute ethanol was obtained from the U. S. Industrial Chemicals Company.

Toluene and methylcyclohexane were further purified by fractional distillation. The fractionating column used was of the silvered, vacuum-jacketed type and having a four foot glass ring packed section with an inside diameter of 10 millimeters. The distillation was carried out under dry nitrogen at atmospheric pressure using a reflux ratio of about fifty to one. Ethanol was purified according to the method described by Fieser[29]. The refractive index of the three materials before and after purification are listed in Table 1.

Table 1. Refractive Index of Purified Materials

	n_D^{20}		
	Before Purification	After Purification	Value Given by A.P.I.[30]
Ethanol	1.36159	1.36139	1.36143
Toluene	1.49665	1.49693	1.49693
Methylcyclohexane	1.42320	1.42311	1.42312

Impurity and Melting Point Determination

The impurity content of the purified material and the melting point of the pure material were determined using the calorimeter according to the method outlined by Rossini[31]. The method assumes that the impurity forms an ideal solution with the liquid phase and is insoluble in the solid phase.

The sample material in the can was first induced to freeze by surrounding the vacuum jacket with a liquid nitrogen bath. Both toluene and ethanol samples started to freeze about 10 degrees below their nominal freezing point. The start of the freezing process was clearly indicated by a sudden rise of the temperature of the sample due to the evolution of heat of fusion. The methylcyclohexane sample had a much slower freezing rate than the other two samples. The start of the freezing process was difficult to notice. After the freezing process was nearly completed, the bath used for heat capacity measurement was set up for the calorimeter and the bath temperature was maintained about a half degree below the temperature of the sample.

The melting process was carried out in the same manner as a heat capacity measurement. A known quantity of heat was added intermittently to the sample. After each heating, the temperature of the sample and the amount of heat input were recorded. Due to the fact that the can contained both liquid and solid phases in the melting process, it usually required more than an hour for the temperature of the sample to become constant, after the heating period.

A plot of the accumulated heat input vs. the temperature of the sample gave two nearly straight lines, one in the melting region and the other in the liquid region. The intersection point of these two lines gave the total heat input value when the solid just completely melted. Any other point on the line of the melting region would have a total heat value less than the total heat input value at the intersection by an amount required to melt the remaining solid at that point. Therefore, if the heat of fusion of that material was known, the per cent of solid melted at that point could be calculated. This method of obtaining the per cent melted data vs. observed temperature of the sample does not require that the sample be completely frozen before starting the melting process.

With certain assumptions regarding the properties of the two phase mixture during melting, it can be shown that the plot of the reciprocal of the per cent melted, $1/B$, vs. observed temperature, t_B, will give a line which can be extrapolated to $1/B = 0$. The temperature corresponding to $1/B = 0$ is the melting point, t_{mp}, of the pure material. Also, it can be shown that the mole fraction, x_2, of the impurity in the sample can be estimated from the following equations

$$x_2 = A \cdot B \cdot (t_{mp} - t_B) \qquad (1)$$

$$A = H_f / R \cdot T_{mp}^2 \qquad (2)$$

where A is called the cryoscopic constant; T_{mp} is the absolute temperature corresponding to t_{mp}; H_f is the heat of fusion.

For ethanol, the heat of fusion, 1200 cal./gm. mole, reported by Kelley[32] was used and the cryoscopic constant was calculated to be 0.0239 using the t_{mp} obtained in this work. For toluene, the heat of fusion, 1586 cal./gm. mole, and the cryoscopic constant, 0.02515, reported by Scott, et al.,[33] were used. For methylcyclohexane, the heat of fusion 1613.4 cal./gm. mole, and the cryoscopic constant, 0.0378, reported by Douslin and Huffman[34] were used. Results are summarized in Table 2.

Table 2. Summary of Purity and Melting Point Determination

Per Cent Melted B	Toluene Obs. Temp. t_B°C.	Mole Fraction Impurity, x_2
15.66	-95.010	0.000073
67.39	-94.998	0.000112
76.62	-94.997	0.000116
86.92	-94.996	0.000109
96.90	-94.996	0.000119
Melting Point of Pure Toluene		-94.991 ± 0.02°C.
Mole Fraction Impurity		0.0001 ± 0.00005

Per Cent Melted B	Methylcyclohexane Obs. Temp. t_B°C.	Mole Fraction Impurity, x_2
19.27	-127.944	0.0105
24.20	-127.651	0.0105
44.34	-127.122	0.0104
59.61	-126.966	0.0105
69.82	-126.893	0.0104
85.12	-126.796	0.0095
Melting Point of Pure Methylcyclohexane		-126.50 ± 0.1°C.
Mole Fraction of Impurity		0.01 ± 0.005

Table 2 - Continued

Per Cent Melted B	Ethanol Obs. Temp. t_B°C.	Mole Fraction Impurity, x_2
10.56	-114.279	0.000427
40.61	-114.194	0.000572
70.70	-114.170	0.000598
90.76	-114.163	0.000600
92.32	-114.160	0.000558
Melting Point of Pure Ethanol		-114.135 ± 0.05°C.
Mole Fraction Impurity		0.0005 ± 0.0001

The melting point of toluene measured in this work is in complete agreement with the value, -94.991 ± 0.012°C., reported by Glasgow, et al.[35]. The same value was selected by A. P. I.[30]. The value, -95.00 ± 0.05°C., reported by Scott, et al.,[33] is also in good agreement with the present value. This indicates that the temperature scale actually realized in the present measurements was in agreement with that of other laboratories also using the international scale.

The freezing point of methylcyclohexane has been reported to be -126.596°C. by Glasgow, et al.,[35] and -126.58 ± 0.05°C. by Douslin and Huffman[34]. The value selected by A. P. I.[30] is -126.593°C. The value reported here is slightly higher. This probably is due to the high impurity content in the sample. It is interesting to notice that even though the methylcyclohexane sample contained one mole per cent of impurity, its refractive index value agreed perfectly with the A. P. I.

value. However, the impurity has no effect on the heat capacity of the material as shown in Chapter IV.

A. P. I.[30] selected the freezing point of ethanol as -114.4°C. with the last significant figure uncertain. Kelley[32] reported the melting point to be -114.6°C. It is believed that the melting point of ethanol has not been accurately measured before. The value reported here is probably the best melting point or triple point of ethanol.

The melting points were measured under a pressure of about 0.5 atm. Since the effect of pressure on the melting point below atmospheric pressure is usually less than the uncertainty of the melting point measured, no correction has been made to the value measured in this work when compared with the freezing point at one atmosphere pressure and triple point reported in the literature.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Calculation of Heat Capacity from Experimental Measurements

The experimentally measured quantities: thermometer resistance, potential measurements across the standard resistor and across the heater resistor, and the measured heating time, were used to determine the heat capacity of the empty can and of the can and sample. These quantities were processed on a Burroughs 220 digital computer using the Burroughs Algebraic Compiler system, taking into account certain corrections outlined below. Various numerical constants and conversions used in the calculation are given in Appendix A.

The heat capacity of the empty can was measured over the range -115°C. to 35°C. These data were corrected for the heat capacity of nitrogen gas in the can, as shown in the sample calculation in Appendix B. The corrected data, given in Table 7, Appendix C., were fitted to a fourth degree polynomial in the temperature by the least-squares method. This polynomial, given in Table 13, Appendix C, was used for interpolation of the heat capacity of the can in the subsequent calculation of the heat capacity of the liquids. When the can contained a liquid sample, the measured heat capacity was a sum of the heat capacity of the can and the sample. The heat capacity of the sample was obtained by subtracting the heat capacity of the can, evaluated at the midpoint

temperature of that measurement, from the measured total heat capacity, of the can plus the sample, as shown in the sample calculation given in Appendix B.

The heat capacity data for each of the pure materials, given in Tables 8, 9, and 10, Appendix C, were also fitted to a polynomial by the least-squares method. These polynomials, given in Table 13, Appendix C, were used to interpolate the heat capacity of the pure material for the calculation of excess heat capacity which is defined by Equation (6), Chapter V. In that calculation, the heat capacity of the pure material was also evaluated at the midpoint temperature of each measurement of the mixture, as shown by the sample calculation in Appendix B.

As described in Chapter II, the contents in the calorimeter can were the liquid sample in equilibrium with a small amount of its vapor and nitrogen gas. The measured heat capacity, after subtracting the heat capacity of the empty calorimeter can, is composed of three parts: the heat capacity of the liquid; the heat capacity of the gas; and the heat required to evaporate some of the liquid into the unfilled space in the can due to the increase of temperature during each measurement. With an unfilled space of about 10 ml. and a temperature of approximately 35°C. (the highest temperature in these measurements), it can be shown that, for the two systems studied here, the magnitude of the last two parts is so small that they can be neglected without affecting the accuracy of the data (see sample calculation in Appendix B).

The liquid sample was filled and sealed in the can with nitrogen gas under atmospheric pressure at room temperature, which varied between

293°K. to 298°K. In this temperature range, the vapor pressure of the liquids studied is less than 80 mm. Hg. pressure. The liquid sample was, therefore, essentially under nitrogen gas pressure. Each heat capacity measurement usually covered less than five degrees; the corresponding pressure change inside the can was estimated to be of less than four per cent in the temperature range studied. The measured heat capacity of the liquids can be regarded as heat capacity measured under constant pressure, C_p, at the pressure of the measurement.

Heat Capacity Data and Discussion

The composition of the samples and the approximate temperature range of the measurements are listed in Table 3.

The heat capacity data of toluene, methylcyclohexane, and ethanol are given in Tables 8, 9, and 10, Appendix C, respectively. The heat capacity data and excess heat capacity data of the ethanol-methylcyclohexane system are given in Table 11, Appendix C, and those of the ethanol-toluene system are given in Table 12, Appendix C. The data points given in each table are listed according to the chronological order of measurement.

The polynomials representing the data of pure materials use t°C. (International Temperature Scale) as the independent variable. The excess heat capacity data of the mixture at each composition were also fitted to a polynomial by the least-squares method using T°K. as the independent variable for the convenience of deriving thermodynamic properties. The conversion to T°K. from t°C. made use of the relation

Table 3. Sample Composition and Temperature Range of Heat Capacity Measurements

System	Composition, Mole Fraction Ethanol	Temperature Range, °C.
Toluene		-95 to 35
Methylcyclohexane		-100 to 35
Ethanol		-110 to 35
Ethanol-Methylcyclohexane	0.3456*	-65 to 35
Ethanol-Methylcyclohexane	0.1979	-65 to 35
Ethanol-Methylcyclohexane	0.8004	-65 to 35
Ethanol-Methylcyclohexane	0.0742	-65 to 35
Ethanol-Methylcyclohexane	0.5324	-65 to 35
Ethanol-Toluene	0.2748	-95 to 35
Ethanol-Toluene	0.6439	-95 to 35
Ethanol-Toluene	0.4505	-95 to 35
Ethanol-Toluene	0.8026	-95 to 35
Ethanol-Toluene	0.0969	-95 to 35
Ethanol-Toluene	0.1841	-95 to 35
Ethanol-Toluene	0.0630	-95 to 35

*Compositions given follow the chronological order of measurement.

T°K. = 273.15 + t°C. The average deviation of experimental data from the polynomials is less than 0.01 cal./gm. mole°C. Only a few exceptional data points show deviations as large as 0.03 cal./ gm. mole°C. All the polynomials are listed in Table 13, Appendix C.

The heat capacity of toluene has been recently measured by Scott, et al.[33]. The accuracy uncertainty of their work was stated to be no greater than 0.2 per cent. The comparison of heat capacity data of this work, calculated from the polynomial given in Table 13, Appendix C, with their data, calculated at the same temperature from

their polynomial, as shown in Table 14, Appendix C, gives a maximum deviation of 0.058 cal./gm. mole°C., or 0.17 per cent, and an average deviation of about 0.03 cal./gm. mole °C.

The heat capacity of methylcyclohexane has been measured by Douslin and Huffman[34], using a calorimeter similar to the one used in this work. Their methylcyclohexane sample had a purity of 99.99 mole per cent. The accuracy uncertainty of their measurement was stated to be no more than 0.2 per cent. The comparison of heat capacity data of this work, calculated from the polynomial given in Table 13, Appendix C, with the experimental data reported by them, as shown in Table 15, Appendix C, gives a maximum deviation of 0.066 cal./gm. mole °C., or 0.16 per cent, and an average deviation of less than 0.02 cal./gm. mole °C. It seems that the higher impurity content of the sample used in this work does not affect the accuracy of the heat capacity data.

The heat capacity of ethanol has not been accurately measured before. The best data until now have been Kelley's 1929 values[32]. The uncertainty of his work in the liquid region was estimated by him to be as large as 1 per cent. The agreement between his work and this work has a maximum deviation slightly larger than 1 per cent.

The heat capacity of the mixtures has not been measured before. However, an indirect check against heat of mixing data in the literature indicates that the excess heat capacity values are generally consistent with good heat of mixing data at different temperatures. Details of the comparison are given in Chapter V.

In view of the reproducibility of the data, the average deviation of the data from the least-squares fitted polynomial, and the agreement with other works in the literature, it is concluded that the accuracy uncertainty in the heat capacity data of both pure material and mixtures is no greater than 0.2 per cent. The uncertainty in the calculated excess heat capacity data is estimated to be less than ± 0.06 cal./gm. mole °C.

CHAPTER V

EXCESS THERMODYNAMIC PROPERTIES OF THE ETHANOL-METHYLCYCLOHEXANE AND ETHANOL-TOLUENE SYSTEMS

Method of Deriving the Excess Properties

The excess thermodynamic properties at the vapor pressure and temperature of the mixture may be defined by the following relations[4]:

$$\left[\begin{array}{l} G^E = G^S - (x_a G_a^o + x_h G_h^o) - RT(x_a \ln x_a + x_h \ln x_h) \\ \quad = G^M - RT(x_a \ln x_a + x_h \ln x_h) \end{array}\right]_{P,T} \tag{3}$$

$$\left[H^E = H^S - (x_a H_a^o + x_h H_h^o) = H^M \right]_{P,T} \tag{4}$$

$$\left[\begin{array}{l} S^E = S^S - (x_a S_a^o + x_h S_h^o) + R(x_a \ln x_a + x_h \ln x_h) \\ \quad = S^M + R(x_a \ln x_a + x_h \ln x_h) \end{array}\right]_{P,T} \tag{5}$$

$$\left[C_P^E = C_P^S - (x_a C_{Pa}^o + x_h C_{Ph}^o) = C_P^M \right]_{P,T} \tag{6}$$

It is shown in Appendix D that the pressure effect on the excess properties can be neglected within the pressure range of this work. The thermodynamic equations relating the excess properties to each other under constant pressure are

$$\left[\frac{\partial H^E}{\partial T} = C_P^E\right]_{P,x} \tag{7}$$

$$\left[\frac{\partial S^E}{\partial T} = \frac{C_P^E}{T}\right]_{P,x} \tag{8}$$

$$[\, G^E = H^E - T\, S^E \,]_{P,T,x} \tag{9}$$

By knowing G^E and H^E at one temperature and C_P^E as a function of temperature for each composition, the excess properties, G^E, H^E, and S^E, in the temperature range of the C_P^E measurements can be calculated using Equations (7), (8), and (9). The polynomials relating excess heat capacity to temperature, given in Table 13, Appendix C, were used in the integration of Equations (7) and (8).

Activity coefficients were computed from the derived value of excess free energy by fitting the isothermal values using the least-squares method to a polynomial of the form*

$$G^E = x_a(1 - x_a)(b_1 + b_2 x_a + b_3 x_a^2 + \cdots) \tag{10}$$

where $b_1, b_2, b_3, \ldots$ are constants at a fixed temperature. The activity coefficients of the alcohol and hydrocarbons are related to the excess free energy by the following relations

$$\left[RT \ln \gamma_a = G^E + x_h \frac{\partial G^E}{\partial x_a}\right]_{P,T,x} \tag{11}$$

$$\left[RT \ln \gamma_h = G^E - x_a \frac{\partial G^E}{\partial x_a}\right]_{P,T,x} \tag{12}$$

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*This equation is equivalent to the Redlich-Kister equation.

Literature Data Used

The integration constants for integrating Equations (7) and (8) have been obtained from the literature. Kretschmer and Wiebe have measured the vapor-liquid equilibrium data of both systems[36,37]. The excess free energy calculated by them from their vapor-liquid data at 308.15°K. was used. The heat of mixing for the ethanol-toluene system has been accurately measured by Brown and Fock[38] and by Mrazek and Van Ness[39]. Brown's data at 308.15°K. agree well with those of Van Ness at the same temperature. Both sets of data were used. For the ethanol-methylcyclohexane system, the heat of mixing of Brown, et al.,[40] were used with corrections made at certain compositions in view of some recent measurements of Brown.* The heat of mixing data and excess free energy values of these two systems at 308.15°K. were smoothed by plotting and interpolated at the compositions corresponding to the heat capacity measurements of the present work. The interpolated values at 308.15°K. are shown in Tables 16 and 17, Appendix E. These values were also used to calculate excess entropy at this temperature.

Results and Discussion

Excess enthalpy, excess entropy, excess free energy, and free energy of mixing were derived at five degree Kelvin intervals starting from 308.15°K. to 188.15°K. for the ethanol-methylcyclohexane system, and from 308.15°K. to 168.15°K. for the ethanol-toluene system. Since the heat capacity for the former system was measured to 208.15°K. and for the latter system was measured to 178.15°K., the properties derived below

*Private communication from Dr. I. Brown, June 11, 1962.

these temperatures were obtained by extrapolation of the polynomials representing the excess heat capacity data. The derived excess properties of ethanol-methylcyclohexane and ethanol-toluene systems are tabulated in Tables 16 and 17, Appendix E. The derived free energy of mixing of the ethanol-methylcyclohexane and ethanol-toluene systems are tabulated in Tables 18 and 19, Appendix E. The variation of H^E, S^E, G^E, and G^M with composition and temperature are shown in Figures 2, 3, 4, and 5, respectively.

Activity coefficients of the ethanol-methylcyclohexane system derived at 308.15°K., 273,15°K., 248.15°K., and 198.15°K. are listed in Table 20, Appendix E. Those of the ethanol-toluene system derived at 308.15°K., 273.15°K., 248.15°K., 223.15°K., 198.15°K., and 173.15°K. are listed in Table 21, Appendix E.

The excess enthalpy of the ethanol-toluene system had been measured by Schulze at 298.15°K.[41] and also by Van Ness at 298.15°K.[42] and at 273.15°K.* The excess enthalpy derived from the present work is slightly higher than Schulze's values. However, the deviation is no more than 5 per cent. The derived values also agree with Van Ness' data at 298.15°K. and 273.15°K. to better than 5 per cent.

The uncertainty in the derived excess properties arise from two sources: one is from the experimental heat capacity data; the other arises from the literature values used here as integration constants. The uncertainty of the excess heat capacity is estimated to be within 0.06 cal./ gm. mole °K. The uncertainty of the excess enthalpy obtained

*Private communication from Dr. H. C. Van Ness, December 31, 1962.

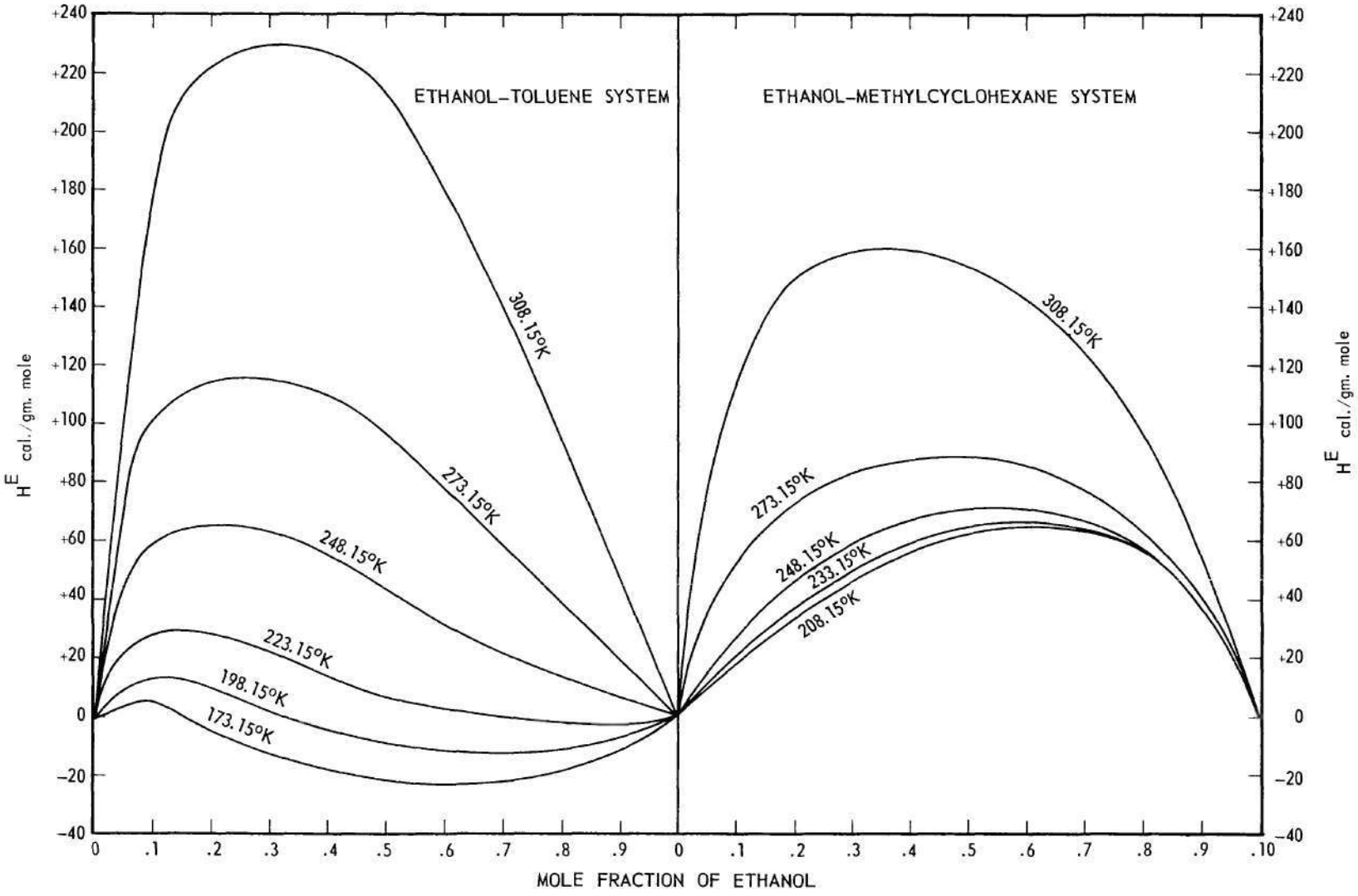

Figure 2. Variation of Excess Enthalpy With Temperature.

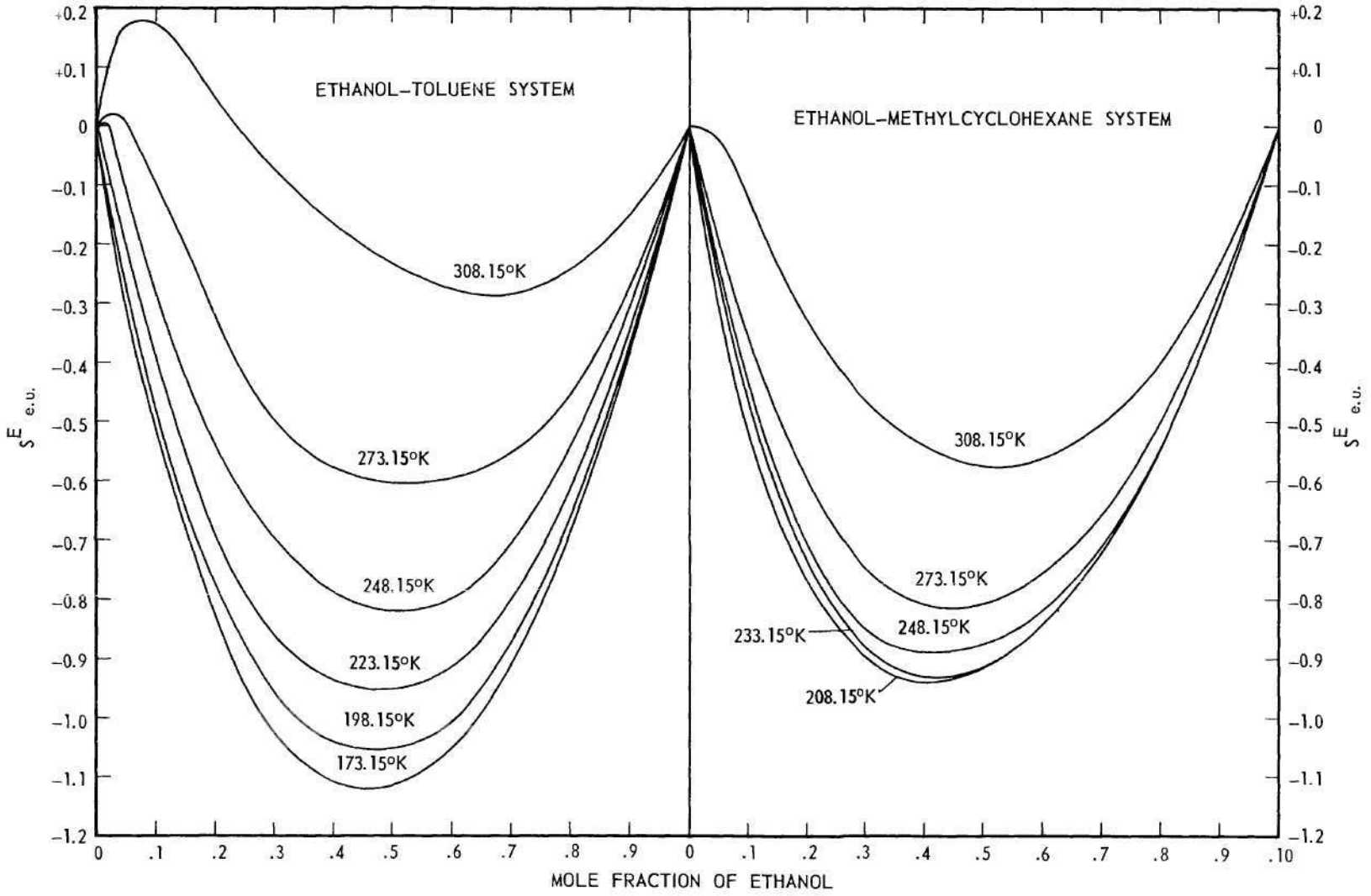

Figure 3. Variation of Excess Entropy With Temperature.

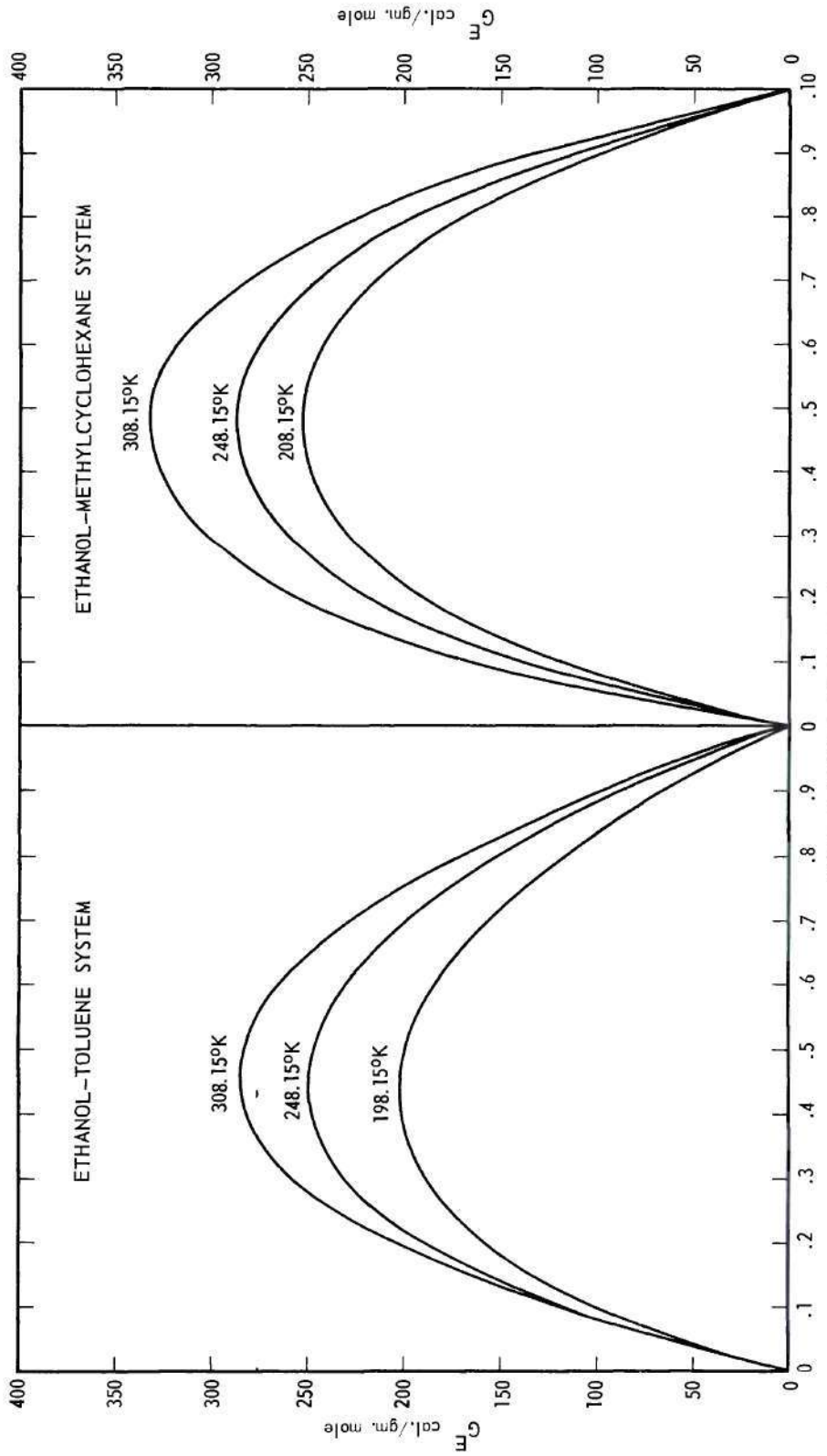

Figure 4. Variation of Excess Free Energy With Temperature.

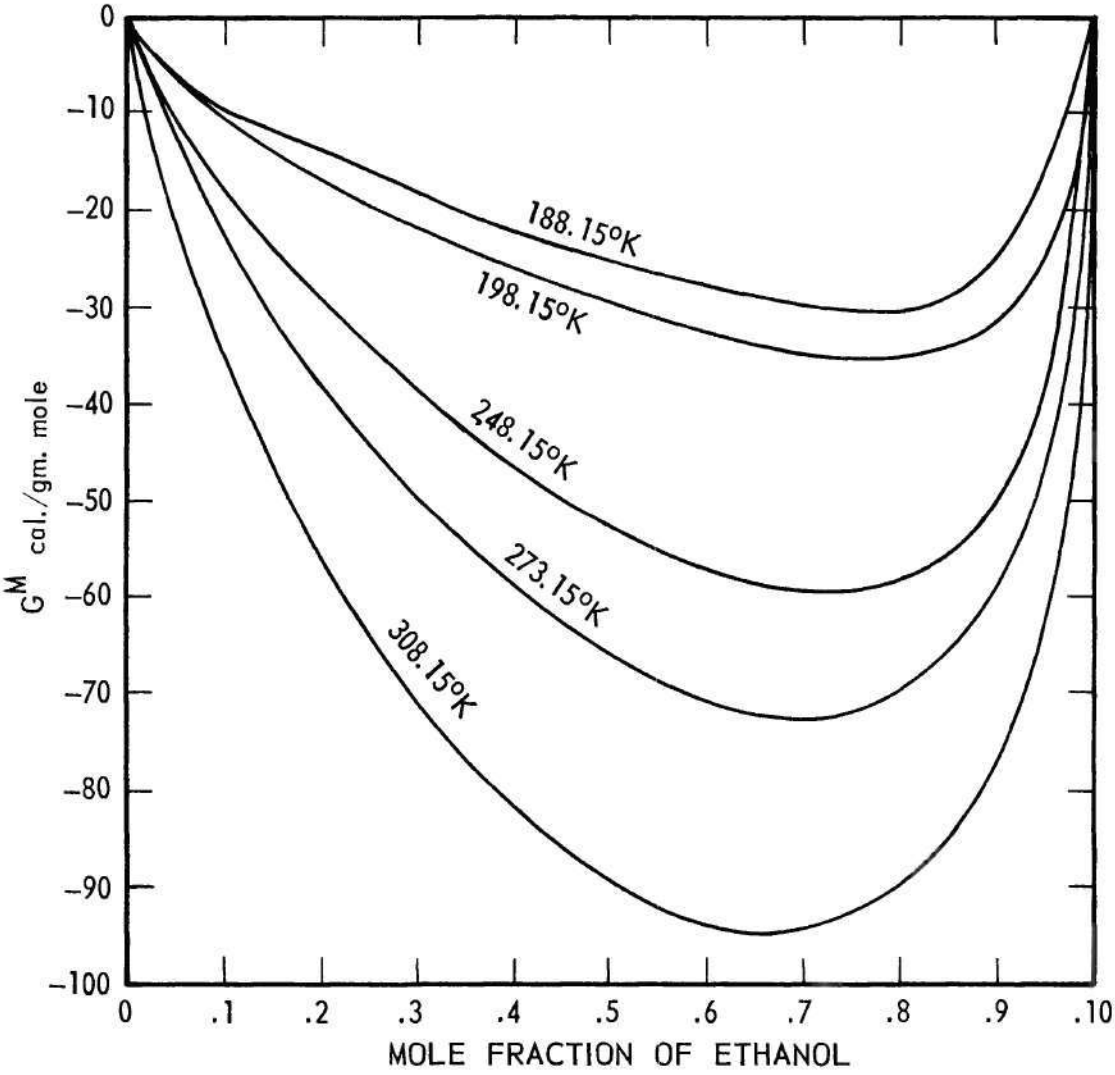

Figure 5. Variation of Free Energy of Mixing With Temperature. Enthanol-Methylcyclohexane System.

from the literature is probably less than 5 per cent. The uncertainty of the excess free energy taken from the literature is believed to be no more than ± 2 per cent. Some of the uncertainty is propagated as the temperature range of the integration is extended. As a rough estimation, the uncertainty of the derived heat of mixing is probably within 10 cal./gm.mole. And the excess entropy and excess free energy are probably accurate to 3 per cent. The accuracy of activity coefficients is not only dependent upon the accuracy of the excess free energy, but also dependent upon the distribution of excess free energy data over the entire concentration range. However, the tabulated activity coefficients should be able to show the temperature effect on the nonideality of the solution.

The excess thermodynamic properties of solutions of alcohols with nonpolar solvents have been studied heretofore mostly near room temperature[24]. The general behavior of the excess thermodynamic properties of the few systems studied in this temperature range, well represented by the ethanol-methylcyclohexane and ethanol-toluene systems (see Figures 2, 3, and 4, $T = 308.15°K.$), can be described as follows. The alcohol-aromatic systems have larger positive excess enthalpy, and less negative excess entropy and lower positive excess free energy than those of alcohol and saturated hydrocarbon or carbon tetrachloride solutions. The excess enthalpy maximum occurs at dilute alcohol compositions for both types of systems. The minimum of the negative excess entropy is, on the contrary, in the concentrated alcohol region. (Actually, for the

alcohol-aromatic solutions, the excess entropy is positive in the dilute alcohol region.) The excess enthalpy and entropy tend to compensate one another so that the excess free energy vs. mole fraction curves are nearly symmetrical for both types of systems.

The explanation for the above mentioned thermodynamic behavior of these systems near room temperature has been summarized by Rowlinson[24] as follows:

1. A major part of the positive excess enthalpy is a measure of the number of hydrogen bonds between alcohol molecules, or other local electrostatic interactions, that are broken on forming the mixture from the pure liquids. That the excess enthalpy is smaller at compositions rich in alcohol can be attributed to fewer hydrogen bonds being broken at these compositions. The small amount of inert diluent is probably accommodated interstitially in a matrix of bonded alcohol molecules without much effect on the hydrogen bonding. The excess enthalpy is large in mixtures dilute in alcohol since the addition of a small amount of alcohol to a large amount of a diluent results in the breaking of most of the hydrogen bonds.

2. The excess entropy is probably positive in mixtures very dilute in alcohol, owing to the loss of orientational order that follows the breaking of the hydrogen bonds originally present in the pure liquid alcohol. This has not been observed experimentally in alcohol and paraffin or carbon tetrachloride solutions; but has been found in alcohol-aromatic solutions. The excess entropy becomes more negative

with increasing concentration of alcohol as the mixture now contains a number of hydrogen bonds which impose both a positional and orientational order on the system that is greater than that to be expected in a randomly dispersed mixture.

3. In the alcohol-aromatic solutions, the interaction between π-electrons of an aromatic molecule and the proton of the hydroxyl group of the alcohol molecule, although not as strong as a conventional hydrogen bond, is less demanding in its geometrical requirements. The interaction between aromatics and alcohols leads to the formation of a weak bond (hereafter called π-bond) as a result, breaking additional hydrogen bonds. This leads to an increase in excess enthalpy and a larger excess entropy compared to those systems involving solvent not having π-electrons.

These theoretical arguments seem to provide a satisfactory explanation for the behavior of these systems near room temperature. Whether or not the same theory can be used consistently to explain the behavior of the two systems studied in this investigation at lower temperatures will now be examined qualitatively.

The temperature dependence of the derived excess thermodynamic properties of the ethanol-methylcyclohexane system are shown in Figures 2, 3, and 4. The excess enthalpy decreases rapidly with lowering of temperature. The rate of decrease falls off with decreasing temperature, becoming negligible below 233°K. Below this temperature the excess enthalpy remains constant with the maximum value being about 40

per cent of that at 308°K. The maximum point shifts to ethanol-rich compositions at low temperatures. The excess entropy becomes more negative with lowering of temperature, but becomes essentially constant below 233°K. The minimum point of excess entropy shifts to methylcyclohexane-rich compositions at low temperatures.

The decrease of excess enthalpy with lowering of temperature may be explained by assuming that fewer hydrogen bonds are broken in the process of forming the solution at the lower temperatures. This will result in more order among the molecules in the solution. The simultaneous decrease of excess entropy supports such an argument. At low temperatures, the excess enthalpy and entropy for a given composition remain essentially constant, suggesting that the breaking of hydrogen bonds no longer contributes significantly to the excess properties. The excess enthalpy in this temperature range may be attributed to the nonideal mixing of the various associated species with hydrocarbon molecules, as the heat of mixing in the regular solutions, for example. The observed constancy of the excess enthalpy for this system at low temperatures suggests that the enthalpy of nonideal mixing may be independent of temperature. In the later discussion, the excess enthalpy not attributed to the breaking of hydrogen bonds will be referred to as the residual excess enthalpy.

For the ethanol-toluene system, the temperature dependence of the excess properties are different from those of the previous system in the following way. With lowering of temperature, the excess enthalpy and

entropy decrease more rapidly and steadily in this system than the ethanol-methylcyclohexane system. The excess enthalpy becomes negative at high alcohol concentration below about 223°K. The rate of decrease of the excess enthalpy below this temperature, though small, is not negligible as shown by the magnitude of the excess heat capacity. The excess entropy of this system, while more positive than that of the previous system near room temperature, decreases rapidly with decreasing temperature, becoming, at the same composition, more negative than that of the ethanol-methylcyclohexane system below 233°K. At low temperatures, the excess enthalpy becomes so small that the magnitude of the excess free energy depends almost entirely upon the excess entropy.

The general trend of decrease of excess enthalpy and entropy with lowering of temperature for the ethanol-toluene system can also be explained, as above, in terms of fewer hydrogen bonds being broken in forming the solution at low temperatures. The additional assumption of the formation of π-bonds is assumed to result in the breaking of more hydrogen bonds in forming the solution; the net effect is expected to be an increase of excess enthalpy and excess entropy. This model gives a satisfactory explanation to the larger excess enthalpy and the less negative excess entropy of this system compared to those of the ethanol-methylcyclohexane system near room temperature. However, this model cannot explain the smaller excess enthalpy and the more negative excess entropy of this system compared to those of the ethanol-methylcyclohexane system at low temperatures, as well as the negative value of the

excess enthalpy of this system in certain composition and temperature range. If the π-bond is assumed to become stronger than the hydrogen bond at low temperatures, it would lead to negative values of the excess enthalpy and excess entropy. However, the excess enthalpy of this system would then be expected to be lower in the dilute alcohol solution, where the formation of π-bond is favored due to the presence of more free hydroxyl groups. This again is contrary to the fact, the excess enthalpy being lower in the concentrated alcohol region. In view of this, it is proposed that the existing model be expanded to include an additional interaction between the toluene molecule and the ethanol species which involves no breaking of hydrogen bonds. The nature of this interaction cannot be deduced from the thermodynamic data; it is postulated to be an interaction between the π-electron and the hydrogen bond. This additional interaction will result in a decrease in the excess enthalpy and because of more orientation order in the solution, a more negative excess entropy.

Generally, polymerization reactions tend to form larger molecular weight species as the reaction temperature decreases. If this is also true for the hydrogen bonding reaction of ethanol, the concentration of free hydroxyl groups in the solution will be expected to decrease with lowering of temperature. Therefore, the effect of forming π-bonds and the effect of breaking hydrogen bonds becomes less important, leaving the interaction between toluene and various ethanol species as a dominant effect at low temperatures. However in the very dilute alcohol

concentration region, where the formation of smaller molecular weight species is more favorable than in other concentration ranges[2], the effect of π-bond formation is shown by a persistently positive excess enthalpy in this concentration range.

The concentration of hydrogen bonds is expected to decrease with increase of temperature at constant composition of solution. Part of the excess heat capacity value can be regarded as the heat absorbed in the breaking of hydrogen bonds during the raising of the temperature of the solution. This explains the behavior of the excess heat capacity of these two systems. The excess heat capacity of these two systems generally increases with the increasing of temperature, indicating that the heat effect due to the breaking of hydrogen bonds is larger at higher temperatures, except in the dilute alcohol ranges of the ethanol-toluene system. For example, the measured excess heat capacity of the ethanol-toluene system at 6.3 mole per cent of ethanol increases with increase of temperature up to about 300°K.; it then drops abruptly with increase of temperature. With the effect of π-bonding, the hydrogen bonds in this dilute alcohol mixture are expected to be nearly all broken at such a high temperature. The further increase of temperature will not cause more hydrogen bonds to break and, therefore, the excess heat capacity decreases above this temperature. The same behavior is expected to occur in the ethanol-methylcyclohexane system at a comparatively higher temperature.

The activity coefficients of the ethanol-methylcyclohexane system (Table 20, Appendix E) increase steadily with decrease of temperature,

and it will probably remain so, as long as the excess enthalpy of this system is positive and large. This indicates the presence of an upper critical solution temperature at lower temperatures. A qualitative cloud point experiment in this work showed that the upper critical solution temperature is about 195°K. with a critical composition in the dilute alcohol concentration. The condition for phase separation to occur is that the free energy of mixing plotted against composition at constant temperature exhibit a common slope at two compositions[43]. From Figure 5, the plot of the free energy of mixing near 190°K. confirms the approximate critical temperature and composition obtained from experiment.

The calculated activity coefficients of the ethanol-toluene system (Table 21, Sppendix E) show a maximum near 223°K; below this temperature, activity coefficients decrease with lowering of temperature. Therefore, the ethanol-toluene system probably does not have an upper critical solution temperature.

CHAPTER VI

THEORY OF ASSOCIATED SOLUTIONS

Introduction

The behavior of the excess properties of the ethanol-methylcyclohexane and ethanol-toluene systems has been discussed qualitatively in Chapter V. Part of the discussion given there is examined quantitatively in this Chapter based on the current theory of associated solutions.

As mentioned in Chapter I, both the theoretical treatment of solutions introduced by Tompa and Barker and the associated theory of solution have been successful in correlating the nonideal behavior of associated solutions. However, the associated theory, based on the chemical association model, is directly pertinent to the qualitative discussion in Chapter V, and is more closely related to the spectroscopic studies of these solutions. Therefore, only the associated theory of solution is used in this work.

The theoretical treatment of the ethanol-methylcyclohexane system, without the complication of other specific interactions such as are present in the ethanol-toluene system, is considerably simpler. Therefore, the theoretical correlation is carried out using mainly the excess properties of the ethanol-methylcyclohexane system. However, the results of the study are extended to the ethanol-toluene system.

Theoretical Background

Due to the formation of hydrogen bonds, alcohol molecules are capable of associating with each other to form linear polymeric species. Pure liquid alcohol can be visualized as a mixture of monomeric alcohol species and polymeric species composed of a different number of units of the alcohol molecule, with the various species at a state of chemical equilibrium. Under this model, the pure liquid alcohol and the alcohol-nonpolar solvent solution both will be treated as a multicomponent system; the only difference is that the solution contains one more component, the solvent, than the pure liquid alcohol.

The development of the associated theory for such alcohol-nonpolar solvent solutions has been essentially based upon the model described above. The theoretical treatment was first developed by Lassettre[16] and then improved by Tobolsky and Blatz[17], Flory[18], Redlich and Kister[19], and Scatchard[20]. Redlich and Kister[19], Kretschmer and Wiebe[21], and Papousek, _et al._,[22] have successfully employed the associated theory to correlate the thermodynamic properties of such solutions. The same model has been used to interpret the results of spectroscopic measurements of such solutions. The work in the field of spectroscopy has been extensively reviewed by Pimentel and McClellan[44]. They have also collected the results from theoretical correlations of both spectroscopic measurements and thermodynamic measurements. Prigogine and Defay[2] have reviewed the development of the associated theory based on both thermodynamic and spectroscopic data. Hildebrand and Scott[45] have also reviewed the development of the associated theory.

The theoretical treatment used in this work is similar to the one used by Kretschmer and Wiebe[21] who have applied the theoretical treatment to the thermodynamic properties of the ethanol-methylcyclohexane system measured at 35°C. and 55°C. The following derivation of the theoretical relations parallel that of Kretschmer and Wiebe; the difference between the two derivations will be pointed out during and after the derivation.

It is assumed that, in the pure ethanol liquid or in the ethanol solutions, the various ethanol species are in equilibrium with each other, for example

$$C_2H_5OH + (C_2H_5OH)_{i-1} \rightleftarrows (C_2H_5OH)_i$$

or

$$\mu_1 + \mu_{i-1} = \mu_i \tag{13}$$

where μ_1 is the chemical potential of the monomeric ethanol species; and μ_i is the chemical potential of the ethanol species which is a linear polymer consisting of i units of monomeric ethanol molecule, sometimes referred to as i-mer.

The macroscopic chemical potential of ethanol in the associated model can be shown to be equal to the chemical potential of monomeric ethanol[2]; that is

$$\mu_a = \mu_1 \tag{14}$$

or at constant temperature and pressure,

$$\overline{G}_a = \overline{G}_1 \tag{15}$$

The only assumption implied in these relations is that the various alcohol species are in chemical equilibrium.

In order to evaluate the partial molal free energy of the monomeric ethanol and the solvent-methylcyclohexane, a hypothetical mixing process is postulated as follows:

1. Initially, each alcohol species is in a pure and ordered (crystalline) state. The solvent is in the pure liquid state. These will be used as standard states.

2. The various pure alcohol species and the pure solvent are then mixed. The amount of each species added to the mixture is equal to the equilibrium composition of the mixture. Therefore, there is no chemical reaction involved in the mixing process and each species acts as if it were a stable compound.

3. There is no volume change during mixing.

4. The heat of mixing of the solvent with various alcohol species can be expressed in the van Laar form

$$H^M = b\, V^S D_h D_a \qquad (16)$$

5. The entropy of mixing takes into account only the effect of the disorientation of the pure species and the difference in size between various species and the solvent.

This mixing process is identical to the one described by Flory[46] for mixing heterogeneous polymers with solvent. The free energy of the solution and the partial molal free energy of each component in the

solution evaluated by him for the polymer case, therefore, can also be applied to this mixing process.

$$G^S = \sum_{i=1}^{i=\infty} n_i G_i^{oo} + n_h G_h^o + b\, V^S D_h D_a \qquad (17)$$

$$+ RT \left\{ N_h \ln D_h + \sum_{i=1}^{i=\infty} \left[N_i \ln \left(D_i / \left(\frac{V_i}{V_h} \right) \right) \right] \right.$$

$$- \sum_{i=1}^{i=\infty} \left[\left((V_i/V_h) - 1 \right) n_i \right] \left[\ln (\theta - 1) - 1 \right]$$

$$\left. + \ln \rho \sum_{i=1}^{i=\infty} n_i \right\}$$

$$\bar{G}_h = G_h^o + RT \left[\ln D_h + D_a - \sum_{i=1}^{i=\infty} \left(D_i / \left(\frac{V_i}{V_h} \right) \right) \right] \qquad (18)$$

$$+ b\, V_h D_a^2$$

$$\bar{G}_i = G_i^{oo} + RT \left[\ln \left(D_i / \left(\frac{V_i}{V_h} \right) \right) + \left(\frac{V_i}{V_h} \right) D_a \right. \qquad (19)$$

$$- (V_i/V_h) \sum_{i=1}^{i=\infty} \left(D_i / \left(\frac{V_i}{V_h} \right) \right) \Big] - (V_i/V_h - 1)$$

$$\left. \cdot \ln (\theta - 1) + \ln \rho \right] + b\, V_i D_h^2$$

Equations (17), (18), and (19) are the relations given by Flory[46] for mixtures of heterogeneous polymers with solvent. When Equation (19) is applied to the monomeric ethanol species in the ethanol-methylcyclohexane system, the following relation is obtained.

$$\bar{G}_i = \bar{G}_a = G_i^{oo} + RT \left[\ln D_i - \ln \frac{V_a}{V_h} + \frac{V_a}{V_h} D_a \right. \tag{20a}$$

$$\left. - V_a \sum_i C_i - \left(\frac{V_a}{V_h} - 1\right) \ln (\theta - 1) + \ln \rho\right] + b\, V_a D_h^2$$

For the monomeric ethanol species in the pure ethanol liquid, the following relation is used

$$\bar{G}_i^o = G_a^o = G_i^{oo} + RT \left[\ln D_i^o - \ln \frac{V_a}{V_h} + \frac{V_a}{V_h} D_a^o \right. \tag{20b}$$

$$\left. - V_a \sum_i C_i^o - \left(\frac{V_a}{V_h} - 1\right) \ln (\theta - 1) + \ln \rho\right]$$

The quantity V_i/V_h is introduced to Equation (19) as a refinement to the lattice model[46]. This quantity which appears as V_a/V_h in Equation (20b) for pure ethanol liquid may be set equal to unity according to the interpretation of Flory[46]. However, this term is retained as it is in Equation (20b) as an approximation.

Consider the excess free energy of the binary mixture

$$G^E = x_a(\bar{G}_a - G_a^o) + x_h(\bar{G}_h - G_h^o) - RT(x_a \ln x_a + x_h \ln x_h) \tag{21}$$

Substitution of Equations (19), (20a) and (20b) into Equation (21), yields for G^E the following relation:

$$G^E = RT \left[x_a \ln \frac{D_i}{D_i^o x_a} + x_h \ln \frac{D_h}{x_h} - (V^S \sum_i C_i \right. \tag{22}$$

$$\left. - x_a V_a \sum_i C_i^o)\right] + b\, V^S D_a D_h$$

In the above equation, the concentration or the volume fraction involving various species are not known quantities, but they can be shown to be related to the stoichiometric alcohol concentration, which is a known quantity, through the following derivation. The equilibrium constants of the association reaction of the ethanol can be obtained from the chemical potential of the reactants and products which are given by Equation (19). After simplification, the equilibrium constants are shown[46] to be

$$K_i = \frac{C_i}{C_1 \cdot C_{i-1}} \cdot \frac{1}{V_a} \tag{23}$$

where K_i is the equilibrium constant for the reaction

$$(C_2H_5OH)_{i-1} + C_2H_5OH \rightleftarrows (C_2H_5OH)_i$$

For the convenience of deriving equations, another equilibrium constant is defined as

$$K_{ci} \equiv \frac{C_i}{C_1 \cdot C_{i-1}} \tag{24}$$

The constant K_{ci} has units of inverse of concentration, while K_i is a dimensionless constant.

The previous works[19,21,22], which have used similar theoretical treatment as described above, have assumed that the equilibirum constants for association reaction between any two species have the same value. Some evidence[21,22,47] has suggested the use of a different constant for the dimerization reaction. Therefore, in the present treatment, it is

assumed that the reaction constants for association reaction other than dimerization have the same value, which will be referred to as K_i or K_{ci}, while the dimerization reaction constant, K_2 or K_{c2}, is not required to be equal to K_i or K_{ci}. The following derivation is based on the presence of two separate constants, K_{c2} and K_{ci}.

The monomeric ethanol concentration can be shown to be related to the stoichiometric ethanol concentration in the following derivation.

$$C_a = \sum_i i\, C_i \tag{25}$$

From Equation (24)

$$C_i = C_1^i\, K_{c2}\, K_{ci}^{i-2} \qquad \text{for } i > 1 \tag{26}$$

Substituting Equation (26) into Equation (25), the following is obtained

$$C_a = \frac{K_{c2}C_1}{K_{ci}} \sum_{i=2}^{i=\infty} i(C_1K_{ci})^{i-1} + C_1 \tag{27}$$

The quantity, C_1K_{ci}, which is equal to C_i/C_{i-1} as shown by Equation (24), is assumed to be less than unity. This seems to be a reasonable choice, since the assumption that $C_1K_{ci} \geq 1$ appears to lead to unrealistic distribution of the polymeric species. With the assumption that $C_1K_{ci} < 1$, and the following well-known relations

$$\sum_i i\,(C_1K_{ci})^{i-1} = \frac{d}{d(C_1K_{ci})} \sum_i (C_1K_{ci})^i \tag{28}$$

$$\sum_{i=1}^{i=\infty} (C_1K_{ci})^i = \frac{C_1K_{ci}}{1 - C_1K_{ci}} \tag{29}$$

Equation (27) can be reduced to the following expression

$$C_a = C_1 \left(\frac{K_{c2}}{K_{ci}} \left(\frac{1}{(1 - C_1 K_{ci})^2} - 1\right) + 1\right) \tag{30}$$

Using the relations given by Equations (26) and (29), the total concentration of various alcohol species, $\sum_i C_i$, can be shown to be

$$\sum_i C_i = \frac{K_{c2} C_1^2}{1 - C_1 K_{ci}} + C_1 \tag{31}$$

For the pure ethanol liquid, C_a, C_1, and C_i in Equations (30) and (31) are replaced by C_a^o, C_1^o, and C_i^o. With C_1 and C_i expressed as a function of C_a, K_{c2}, and K_{ci}, the G^E in Equation (22) becomes a function of temperature, concentration of the solution, molal volume of pure ethanol and methylcyclohexane, and the parameters b, K_{c2}, and K_{ci}.

The excess enthalpy of mixing, H^E, is visualized as being composed of two parts:

1. The heat of mixing which originates from the mixing of various species with methylcyclohexane molecules, H^E_{residual}; and

2. The heat effect due to the breaking or forming of hydrogen bonds, $H^E_{\text{bond rupture}}$. That is

$$H^E = H^E_{\text{residual}} + H^E_{\text{bond rupture}} \tag{32}$$

The first part is related to the dispersion forces in the liquid mixture and is assumed not to be affected by the distribution of polymeric species, being related only to the macroscopic concentration of the solution. Therefore, this portion of the heat of mixing is set equal to the heat of mixing assumed in Equation (16), i.e.,

$$H^{E}_{\text{residual}} = b\, V^{S} D_a D_h \tag{33}$$

The second part of the excess enthalpy, $H^{E}_{\text{bond rupture}}$, resulted from the redistribution of various ethanol species during the mixing process, and was obtained from the following derivation:

Let H^{R}_{2} be the enthalpy of formation of the dimer bond,

$$C_2H_5OH + C_2H_5OH \rightarrow (C_2H_5OH)_2$$

and H^{R}_{i} be the enthalpy of formation of any other hydrogen bond,

$$(C_2H_5OH)_j + (C_2H_5OH)_{i-j} \rightarrow (C_2H_5OH)_i \qquad i \neq 2$$

From Equation (24), the number of moles of dimer bond in x_a moles of pure ethanol liquid is given by $V_a x_a K_{c2} (C^{o}_{1})^2$ and the number of moles of dimer bond in one mole of solution of composition x_a is given by $V^{S} K_{c2} (C_1)^2$. Thus, the number of moles of dimer bond broken in forming the solution is

$$n_{\text{dimer bond rupture}} = V_a X_a K_{c2} (C^{o}_{1})^2 - V^{S} K_{c2} (C_1)^2 \tag{34}$$

The concentration of hydrogen bonds in a liquid containing various ethanol species is

$$C_{\text{hydrogen bond}} = \sum_i (i - 1)C_i = \sum_i i\, C_i - \sum_i C_i \qquad (35)$$

Substituting Equations (25), (30), and (31) into Equation (35), gives

$$C_{\text{hydrogen bond}} = K_{ci}\, C_1\, (C_a - C_1) + K_{ci}(C_1)^2 \qquad (36)$$

The total number of moles of various hydrogen bonds in x_a moles of pure ethanol liquid is $V_a x_a C^o_{\text{hydrogen bond}}$ and those in one mole of solution of composition x_a is $V^S C_{\text{hydrogen bond}}$. Therefore, the number of moles of hydrogen bond, excluding the dimer bond, ruptured in forming the solution is

$$n_{\text{i-mer bond rupture}} = V_a x_a\, C^o_{\text{hydrogen bond}} - V^S\, C_{\text{hydrogen bond}} - n_{\text{dimer bond rupture}} \qquad (27)$$

or from Equations (34) and (36)

$$n_{\text{i-mer bond rupture}} = x_a\, K_{ci}\, C^o_1 (1 - V_a C^o_1) - K_{ci}\, C_1 (x_a - V^S C_1) \qquad (38)$$

The total enthalpy effect from breaking of hydrogen bonds is

$$H^E_{\text{bond rupture}} = -H^R_2 \cdot n_{\text{dimer bond rupture}} - H^R_i \cdot n_{\text{i-mer bond rupture}} \qquad (39)$$

In the case that H_2^R is equal to H_1^R, as it was assumed in the qualitative correlation given later, then

$$H^E_{\text{bond rupture}} = -H_i^R \cdot (n_{\text{dimer bond rupture}} + n_{\text{i-mer bond rupture}}) \tag{40}$$

From Equations (32), (33), and (39), the total excess enthalpy of the solution is found to be

$$H^E = b\, v^S D_a D_h - H_2^R \cdot K_{c2} [V_a x_a (C_1^o)^2 - V^S (C_1)^2] - H_i^R [x_a K_{ci} C_1^o (1 - V_a C_1^o) - K_{ci} C_1 (x_a - V^S C_1)] \tag{41}$$

The previous derivations are essentially parallel to those of Kretschmer and Wiebe[21] with the exception of the following changes:

1. A slightly different standard state is used for the pure polymeric species. This change provides a more consistent derivation for the equilibrium constant[46], while Kretschmer and Wiebe found it necessary to introduce a term into the chemical equilibrium relation in order to obtain the correct expression - Equation (23). However, Equations (22) and (41) are not affected by this change.

2. A separate equilibrium constant is used in this work to characterize the dimerization reaction.

3. The enthalpy of reaction is used instead of the energy of reaction in order to avoid the correction of the enthalpy of mixing to the energy of mixing.

After taking into consideration the above mentioned changes, all the equations derived here can be reduced to the corresponding ones of Kretschmer and Wiebe[21], and of Papousek, et al.,[22] whose derivation is identical with that of Kretschmer and Wiebe.

The above derivation follows entirely the description of the ethanol-methylcyclohexane system, so these relations are expected to be applicable only to this system and the related systems such as, for example, alcohol-saturated hydrocarbon systems or alcohol-carbon tetrachloride systems. For the ethanol-toluene system, the hydrogen bond part can be treated in the same manner as the ethanol-methylcyclohexane system. The π-bonding may be treated as compound formation between toluene molecules and alcohol species.

The additional interaction between toluene molecules and ethanol species, proposed in this work, will be expected to contribute both a negative excess entropy term and a negative excess enthalpy term; the magnitude of these two terms is expected to be not significantly affected by the distribution of the polymeric ethanol species, but to be affected mainly by the macroscopic concentration of the solution.

The derivation of the theoretical treatment for the ethanol-toluene system will be expected to be similar to the derivations given for the ethanol-methylcyclohexane system with the exception of:

1. having additional equilibrium relations between the π-bond concentration, the concentration of the free (not already bonded) toluene molecules and the concentration of the free proton of the hydroxyl group;

2. adding a negative enthalpy term and a negative entropy term in the derivation of equations corresponding to Equations (17), (18), and (19); and

3. Including the negative excess enthalpy effect of both the π-bond formation, $H^E_{\pi\text{-bonding}}$, and the additional interaction between toluene and ethanol species, $H^E_{\text{interaction}}$, into the residual excess enthalpy in addition to the portion of residual excess enthalpy contributed from the dispersion forces, $H^E_{\text{dispersion}}$, corresponding to the term defined by Equation (16) or Equation (33) for the ethanol-methylcyclohexane system.

The excess enthalpy of the ethanol-toluene system, therefore, may be expressed as

$$H^E = H^E_{\text{residual}} + H^E_{\text{bond rupture}} \tag{42}$$

where

$$H^E_{\text{residual}} = H^E_{\pi\text{-bonding}} + H^E_{\text{interaction}} + H^E_{\text{dispersion}} \tag{43}$$

Kretschmer and Wiebe[21], on the other hand, have assumed that each aromatic molecule can combine with one molecule of alcohol species and that the nonideal mixing between the ethanol species and the toluene molecule is simply a quantity given by Equation (16). Their theoretical treatment might be expected to have difficulties in correlating both the excess free energy data and the excess enthalpy data of the ethanol-toluene system.

Method of Calculation of Parameters

The purpose of this section is to examine whether Equations (22) and (41) can properly correlate the experimentally derived excess free

energy and excess heat of the ethanol-methylcyclohexane system, and to obtain the value of the parameters b, K_{c2}, K_{ci}, H_2^R, and H_i^R. If Equations (22) and (41) are indeed a correct description of the system, it should be possible to correlate the derived excess free energy and excess enthalpy at constant temperature but different composition. The calculation is, therefore, essentially a search for such a set of parameters for each temperature, using the derived excess free energy and excess enthalpy data at this temperature.

All the volume fractions and concentrations used in the calculation were obtained from mole fraction data by neglecting the volume of mixing. The density of methylcyclohexane reported by A. P. I.[30] and the density of ethanol measured by Körber[48] were used.

The detailed method of calculation is given in Appendix F. The calculation is summarized below.

Equation (22), containing only three parameters b, K_{c2}, and K_{ci}, is simpler to use as the starting point of the calculation than Equation (41), which contains all five parameters to be determined. If b is known, Equation (22) can be used to obtain by successive iteration the best value of K_{c2} and K_{ci} which will provide Equation (22) the closest fit to the derived excess free energy data. After several tries, it was found possible to select a value for b which enabled Equation (22) to reproduce the experimentally derived excess free energy to an accuracy within the uncertainty of the derived values. The deviation between the calculated and the derived values is fairly sensitive to the

choice of b, a variation of less than 20 per cent from the best value of b being sufficient to make the deviation larger than the uncertainty of the derived values. For each b thus determined, there exists a definite relation between K_{c2} and K_{ci}; each pair of K_{c2} and K_{ci} that satisfies the relation will fit the derived excess values equally well. To find a unique pair of equilibrium constants it was necessary to examine the resulting agreement with derived excess enthalpy data.

With b already known, several pairs of K_{c2} and K_{ci}, which satisfied the previously determined excess free energy relation, were tried in Equation (41). H_2^R and H_i^R were determined for each pair of equilibrium constants by the least-squares method using the derived excess enthalpy data. The deviation of the derived excess enthalpy from the excess enthalpy calculated by Equation (33), using the enthalpy of formation values obtained by the least-squares method, was in all cases less than the uncertainty of the derived excess heat. It was found that the value of H_i^R was not sensitive to the choice of equilibrium constants; while the value of H_2^R was very sensitive to this choice.

The value of H_2^R was expected to be reasonably close to the value of H_i^R. Therefore, the agreement between the values of H_2^R and H_i^R was used as a criterion for selecting a unique pair of equilibrium constants. The previously described method was used to correlate the derived excess free energy data and the excess enthalpy data at 308.15°K., 273.15°K., 248.15°K., 223.15°K., and 198.15°K. When the derived excess enthalpy at lower temperatures, 223.15°K. and 198.15°K., was used in the

correlation, it was found that the excess enthalpy contributed by the breaking of hydrogen bonds was negligible in this temperature range. As far as the determination of the enthalpy of formation of hydrogen bonds is concerned, Equation (41) is ineffective in the low temperature range. Therefore, the enthalpy of bond formation, H_i^R, at 223.15°K. and 198.15°K was obtained by what appeared to be a reasonable extrapolation of H_i^R, obtained at 308.15°K., 273.15°K., and 248°K. The equilibrium constants at these two lower temperatures were calculated from Equation (44) using the equilibrium constant at 248.15°K. and the extrapolated H_i^R.

$$\frac{\partial \ln K_i}{\partial T} = \frac{H_i^R}{RT^2} \tag{44}$$

Results and Discussion

The parameters determined according to the method described above are listed in Table 4.

Table 4. The Parameters Determined for the Ethanol-Methylcyclohexane System

Temp. °K.	b cal./liter	K_2	K_{c2} liter/gm.mole	K_i	K_{ci} liter/gm.mole	H_i^R cal./gm.mole
308.15	2800	11	0.65	74	4.4	-3590
273.15	2900	21	1.2	131	7.5	-1777
248.15	2950	36	2.0	188	10.5	-942
223.15	3100	(48)*	(2.6)	(221)	(12.0)	(-650)
198.15	3200	(62)	(3.3)	(255)	(13.5)	(-500)

*Values in parentheses have been obtained by extrapolation (see Appendix F).

The uncertainty in b is less than 20 per cent. Above 248.15°K., the uncertainty is probably within 30 per cent for K_2 and K_i, within 20 per cent for H_i^R. The value of H_2^R was arbitrarily chosen equal to H_i^R. Below 248.15°K. the equilibrium constants and enthalpy of reaction, calculated from extrapolation, probably are correct in order of magnitude. However, these sets of parameters have good internal consistency; that is, using these parameters in Equations (22) and (41), one can calculate excess free energy and excess enthalpy values which agree with the derived values to within the uncertainty of the derived values. Also the temperature dependence of the equilibrium constants follows the thermodynamic relation, Equation (44), fairly well. A comparison of the calculated excess values and the derived excess values is given in Table 24, Appendix F.

It is interesting to notice that the parameter b at 308.15°K. reported here (2800 cal./liter) agrees with the value (2980 cal./liter) reported by Kretschmer and Wiebe[21] within the uncertainty of the value.

In terms of empirical fitting of the excess properties, the merit of using two different equilibrium constants instead of one is as follows:

1. Using two constants, Equation (22) can fit the excess free energy data with much smaller values for both constants than the single constant. When the constant is large, as the magnitude reported by Kretschmer (K = 170 at 308.15°K.), the excess free energy is not sensitive to the variation of the constant. At 308.15°K., use of either one or two constants gives an equally good correlation with the measured

excess free energy. At lower temperatures, the one-constant equation is unable to predict the large excess free energy.

2. The one-constant equation can correlate the measured excess enthalpy data at 308.15°K. at best with a deviation of about 15 per cent; while the two-constant equation can correlate to within 2 per cent.

The molar enthalpy of formation of hydrogen bonds (i.e., H_i^R) reported by different workers, using spectroscopic or other measurements, show considerable scattering among the data. The value of H_i^R (3590 cal./gm.mole) found at 308.15°K. agrees fairly well with the average value reported in the literature[49]. The H_i^R obtained at the low temperatures and the temperature dependence of H_i^R appear not to have been measured before. The dimerization equilibrium constant K_{c2} has been reported by Becker[50] from infrared studies to be about 0.45 and 2.0 liter/gm.mole at 308.15°K. and 273.15°K. respectively; the values found in the present work are 0.65 and 1.2 respectively.

The spectroscopic study of such solutions does provide more concrete evidence for certain specific interactions; but the quantitative interpretation of such study is also subject to large uncertainty[49]. Besides, the spectroscopic study alone cannot reveal all the contributions to the nonideal behavior of the solution. A combined study with different methods is again emphasized.

The excess enthalpy resulting from the breaking of hydrogen bonds, $H^E_{\text{bond rupture}}$, and the residual excess enthalpy, H^E_{residual}, calculated from Equations (39) and (33) using the parameters listed in Table 4, are tabulated in Table 5.

Table 5. Residual Excess Enthalpy and Excess Enthalpy from the Breaking of Hydrogen Bonds

x_a	Temp. 308.15°K. $H^E_{residual}$ * cal./gm. mole	Temp. 308.15°K. $H^E_{bond\ rupture}$ ** cal./gm.mole	Temp. 273.15°K. $H^E_{residual}$ cal./gm.mole	Temp. 273.15°K. $H^E_{bond\ rupture}$ cal./gm.mole
0.0742	11.8	99.3	11.9	34.5
0.1979	29.5	118.6	29.5	40.8
0.3456	49.4	114.0	46.1	39.2
0.5324	58.0	92.1	58.0	32.3
0.8004	46.9	45.2	46.8	16.0

x_a	Temp. 248.15°K. $H^E_{residual}$ cal./gm.mole	Temp. 248.15°K. $H^E_{bond\ rupture}$ cal./gm.mole	Temp. 223.15°K. $H^E_{residual}$ cal./gm.mole	Temp. 223.15°K. $H^E_{bond\ rupture}$ cal./gm.mole
0.0742	11.8	14.8	12.0	9.4
0.1979	29.2	17.7	29.9	11.3
0.3456	45.7	17.3	46.9	11.2
0.5324	57.5	14.4	58.8	9.4
0.8004	46.3	7.1	47.4	4.7

x_a	Temp. 198.15°K. $H^E_{residual}$ cal./gm.mole	Temp. 198.15°K. $H^E_{bond\ rupture}$ cal./gm.mole
0.0742	12.0	6.7
0.1979	30.2	8.2
0.3456	47.0	8.2
0.5324	59.2	6.9
0.8004	47.7	3.4

*These values, cal./gm.mole of solution, are calculated from Equation (33) using the same parameters as given in Table 4.

** These values, cal./gm.mole of solution, are calculated from Equation (39) using the same parameters as given in Table 4.

The number of moles of dimer bonds broken, $n_{\text{dimer bond rupture}}$, and the number of moles of other hydrogen bonds broken, $n_{\text{i-mer bond rupture}}$, calculated from Equations (34) and (38) using the parameters listed in Table 4, the total number of moles of hydrogen bonds broken and the number of moles of bond rupture per mole of ethanol in the solution are given in Table 6.

Tables 5 and 6 indicate that, below 223.15°K., the heat effect arising from the breaking of hydrogen bonds is indeed negligible as is deduced from the qualitative analysis given in Chapter V. The decrease of this heat effect is, however, not only due to fewer hydrogen bonds being broken but also due to a decrease of H_i^R. The residual excess enthalpy is essentially temperature independent. Table 6 also indicates that there are comparatively more hydrogen bonds broken in the dilute alcohol region than in the concentrated region, considering the number of moles of ethanol in the solution. Therefore, the qualitative description of the ethanol-methylcyclohexane system in Chapter V is confirmed by the quantitative results obtained in this Chapter.

Since the equilibrium constants and the enthalpy of formation of hydrogen bonding between ethanol molecules are expected to be very nearly the same regardless of the other component of the binary solution, the same value of K_{c2}, K_{ci}, and H_i^R obtained for the ethanol-methylcyclohexane system may also be applied to the ethanol-toluene system. Using these parameters and Equation (36), the heat required for breaking all the hydrogen bonds originally present in 0.063 mole of pure ethanol at

Table 6. Number of Hydrogen Bonds Broken in Forming the Solution

x_a	$n_{\text{dimer bond rupture}}$*	$n_{\text{i-mer bond rupture}}$**	Total Bond rupture***	Total Bond rupture/mole of Ethanol****
	Temperature 308.15°K.			
0.0742	-0.002289	0.029967	0.027678	0.373
0.1979	-0.002539	0.035595	0.033056	0.167
0.3456	-0.002251	0.034011	0.031760	0.0918
0.5324	-0.001689	0.027348	0.025659	0.0482
0.8004	-0.000747	0.013340	0.012593	0.0157
	Temperature 273.15°K.			
0.0742	-0.001627	0.021093	0.019466	0.262
0.1979	-0.001675	0.024232	0.022557	0.114
0.3456	-0.001453	0.023541	0.022088	0.0639
0.5324	-0.001075	0.019290	0.018215	0.0342
0.8004	-0.000471	0.009477	0.009006	0.0112
	Temperature 248.15°K.			
0.0742	-0.001412	0.017155	0.015743	0.212
0.1979	-0.001420	0.020233	0.018813	0.0950
0.3456	-0.001223	0.019622	0.018399	0.0532
0.5324	-0.000902	0.016206	0.015304	0.0287
0.8004	-0.000394	0.008025	0.007631	0.00953
	Temperature 223.15°K.			
0.0742	-0.001382	0.015877	0.014495	0.195
0.1979	-0.001382	0.018905	0.017523	0.0885
0.3456	-0.001188	0.018487	0.017299	0.0500
0.5324	-0.000876	0.015339	0.014463	0.0271
0.8004	-0.000383	0.007630	0.007247	0.00905

continued next page

*For footnotes, see next page.

Table 6 - continued

x_a	$n_{\text{dimer bond rupture}}$*	$n_{\text{i-mer bond rupture}}$**	Total Bond rupture***	Total Bond rupture/mole of Ethanol****
	Temperature 198.15°K.			
0.0742	-0.001359	0.014886	0.013527	0.182
0.1979	-0.001355	0.017885	0.016530	0.0835
0.3456	-0.001163	0.017619	0.016456	0.0476
0.5324	-0.000857	0.014678	0.013821	0.0259
0.8004	-0.000375	0.007330	0.006955	0.00869

*These values, gm.mole of dimer bond rupture/gm.mole of solution, are calculated from Equation (34) using the parameters given in Table 4. The minus sign indicates the formation of dimer bonds.

**These values, gm.mole of i-mer bond rupture/gm.mole of solution, are calculated from Equation (38) using the parameters given in Table 4.

***These values, gm.mole of bond rupture/gm.mole of solution, are calculated by adding the values in column 2 to the values in column 3 of the same composition.

****These values, gm.mole of bond rupture/gm.mole of ethanol in solution, are calculated by dividing the values in column 4 by the corresponding x_a in column 1.

308.15°K. is estimated to be about 200 cal. The excess enthalpy, H^E, of the ethanol-toluene system at 308.15°K. and at a concentration of 0.063 mole fraction of ethanol, is 142 cal./gm.mole. According to the discussion given in Chapter V, the term, H^E_{residual}, in Equations (42) and (43) is negative in low temperatures. This term is likely to be also negative near room temperature. If this is the case, the term, $H^E_{\text{bond rupture}}$, at this temperature and composition will be larger than

142 cal./gm.mole which is already 70 per cent of the enthalpy required to break all the hydrogen bonds. This indicates that the hydrogen bond in this solution is indeed mostly broken, as is deduced in Chapter V from the behavior of the excess heat capacity. For the ethanol-methylcyclohexane system at the same temperature and composition, the excess enthalpy contributed from the breaking of bonds is about 90 cal./gm. mole (estimated from the values given in Table 5) indicating that only about half of the hydrogen bonds originally present in pure ethanol liquid are broken in this solution.

The large reaction equilibrium constants and the small magnitude of the enthalpy of formation of the hydrogen bonding at low temperatures indicate that the heat effect arising from the breaking of hydrogen bonds may be expected to be generally small for the alcohol-hydrocarbon systems at these temperatures. Studying the excess enthalpy of these systems at low temperatures can, therefore, reveal enthalpy effects other than those from the breaking of hydrogen bonds. On the other hand, the excess properties at high temperatures can provide a more effective correlation for the associated theory of solutions in addition to the fact that it can show the profound effect of the breaking of hydrogen bonds.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

The work done in this study may be summarized as follows:

1. The heat capacity of the three pure liquids, toluene, methylcyclohexane, and ethanol, were measured in the temperature range from 35°C. to -95°C., 35°C. to -100°C., and 35°C. to -110°C., respectively. The heat capacity measurements of the ethanol-methylcyclohexane system were made over the temperature range of 35°C. to -65°C. at the following compositions: 0.0742; 0.1979; 0.3456; 0.5324; and 0.8004 mole fraction of ethanol. The heat capacity measurements of the ethanol-toluene system were made over the temperature range of 35°C. to -95°C. at the following compositions: 0.0630; 0.0969; 0.1841; 0.2748; 0.4505; 0.6439; and 0.8026 mole fraction of ethanol.

2. The expreimental heat capacity data were used to compute the excess heat capacity. The excess heat capacity data were used to derive excess thermodynamic properties, G^E, H^E, S^E, and G^M at five degree intervals from 35°C. to -85°C. for the ethanol-methylcyclohexane system, and from 35°C. to -105°C. for the ethanol-toluene system. The activity coefficients were calculated at 0°C., -25°C., -50°C., and -75°C. for the ethanol-methylcyclohexane system, and at 0°C., -25°C., -50°C., -75°C., and -100°C. for the ethanol-toluene system.

3. The quantitative treatment used by Kretschmer and Wiebe[21] was redeveloped in this work to include two equilibrium constants, one for

the dimerization reaction and the other for the association reaction other than dimerization, instead of using a single equilibrium constant for all the association reaction.

4. The above mentioned theoretical treatment was used to correlate the derived values of G^E and H^E of the ethanol-methylcyclohexane system at 35°C., 0°C., -25°C., -50°C., and -75°C. The parameters used in the present treatment: the enthalpy of formation of the hydrogen bonds, H_i^R,; the heat of mixing due to nonideal mixing between the ethanol species and the methylcyclohexane molecules, b; the equilibrium constant for the dimerization reaction, K_2 or K_{c2}; the equilibrium constant for association reaction other than dimerization, K_i or K_{ci}, were estimated at 35°C., 0°C., -25°C., -50°C., and -75°C.

Conclusions

From the experimental measurements the following conclusions can be drawn:

1. The purity of the toluene, ethanol, and methylcyclohexane samples used in this work was judged to be of adequate purity as shown by calorimetric melting point determinations. The melting point and purity measurements of toluene indicated that the temperature scale actually realized in the present measurements was in agreement with that of other laboratories also using the international scale. The purity and melting point measurements of ethanol resulted in a melting point of -114.135°C. which is believed to be more accurate than other reported values.

2. Where comparisons could be made, the heat capacity measurements obtained in this work are in good agreement with previously reported data of high accuracy. The accuracy uncertainty of the heat capacity data is estimated to be within 0.2 per cent. The accuracy uncertainty of the excess heat capacity data is probably within 0.06 cal./gm.mole °C.

From a study of the derived thermodynamic properties of these two systems, the following conclusions can be drawn:

1. The temperature dependence of the excess properties of the ethanol-methylcyclohexane system suggests that the number of hydrogen bonds broken in the forming of solution decreases with lowering of temperature, that the contribution to the excess enthalpy from the breaking of hydrogen bonds becomes insignificant at low temperatures, and that the enthalpy effect from the nonideal mixing between ethanol species and methylcyclohexane molecules becomes dominant at low temperatures; this enthalpy effect appears to be temperature independent.

2. The temperature dependence of the excess properties of the ethanol-toluene system suggests that the contribution to the excess enthalpy arising from the breaking of hydrogen bonds also decreases with lowering of temperature. Postulation of an additional interaction between the toluene molecule and the ethanol species (assumed not to affect the equilibrium distribution of the ethanol species) to the current theory of such solutions provides a model consistent with the behavior of this system.

From the theoretical treatment of the ethanol-methylcyclohexane system the following conclusions can be drawn:

1. It was found that the treatment developed in this work could correlate the derived excess free energy and excess enthalpy data at each temperature to within the uncertainty of the derived data; while the treatment used previously by other workers cannot correlate satisfactorily the excess enthalpy data and the excess free energy data at low temperatures.

2. The present treatment showed that: the contribution to the excess enthalpy arising from the breaking of hydrogen bonds decreased with lowering of temperature and became negligible below -40°C.; both the number of hydrogen bonds being broken and the enthalpy of breaking the bonds decreased with lowering of temperature; the heat of mixing due to nonideal mixing ($H^{E}_{residual}$) between ethanol species with methylcyclohexane molecules was essentially temperature independent.

3. The quantitative results obtained from correlation of the isothermal excess thermodynamic properties with composition is consistent with the results obtained by qualitative analysis of the temperature dependence of the excess thermodynamic properties; indicating that the theoretical model used is properly describing the behavior of the solution.

4. The results obtained from the theoretical treatment of the ethanol-methylcyclohexane system substantiate part of the qualitative analysis made on the ethanol-toluene system.

Recommendations for Future Work

1. The excess thermodynamic properties of these two systems at temperatures higher than the temperature range studied in this work are recommended for future study mainly for the following reasons:

a. The results of this work suggest that the excess enthalpy of the ethanol-toluene system will be much less temperature dependent at temperatures above the temperature range of this work; the same behavior will be expected for the ethanol-methylcyclohexane system at even higher temperatures. Under such circumstances, the excess enthalpy and excess free energy of the former system are expected to be less than those of the later system. It will be interesting to see whether these predictions agree with the facts.

b. The excess properties at high temperatures can provide more effective correlation to the theoretical treatment and possibly can yield parameters with less uncertainty.

2. The correlation of the excess thermodynamic properties of the ethanol-toluene system is recommended for study according to the suggested model.

3. In order to verify that the behavior of these two systems are indeed representative of the two kinds of solutions, namely the alcohol-saturated hydrocarbon and the alcohol-unsaturated hydrocarbon solutions, some other solutions of similar kinds, for example ethanol-isooctane and ethanol-hexene, should be studied.

4. Certain properties of the theoretical model can be examined more directly by spectroscopic methods than a thermodynamic approach.

Therefore, the spectroscopic study of these two systems covering the same temperature range is also recommended for future study.

A P P E N D I C E S

APPENDIX A

NUMERICAL CONSTANTS AND CONVERSIONS USED IN CALCULATIONS

Temperature Scale

All the temperature measurements were made with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards on the International Temperature Scale; these temperature measurements are reported here in degrees centigrade. The data used for deriving excess thermodynamic properties were converted to the Kelvin scale by the following relation

$$T°K. = 273.15 + t°C.$$

Molecular Weights

The molecular weights of the substances studied in this research were calculated based on the atomic weights published in 1952 [51], which gave the following atomic weights:

oxygen 16

hydrogen 1.0080

carbon 12.010

The molecular weights calculated from the above atomic weights are:

ethanol 46.068

toluene 92.134

methylcyclohexane 98.182

Energy Conversion

All electrical measurements were in absolute units. The calculated energy in absolute joules was converted to defined calories by the following relation

1 defined calorie = 4.1840 absolute joules

The calorie used in this research is the defined calorie.

APPENDIX B

CALCULATION OF HEAT CAPACITY FROM MEASURED DATA

Sample Calculation for the Heat Capacity of the Calorimeter Can

The following data were obtained during a particular measurement:

1. Initial resistance readings from the Mueller bridge (same as the final readings taken in the preceding measurement) were N = 25.8283 ohms, R = 25.8285 ohms.

2. In the middle of the heating period, the potential reading, P, across the volt box, and the potential reading, Q, across the one ohm standard resistor, were 0.038464 and 0.051937 absolute volts, respectively.

3. The heating interval, S, was 689.8 seconds.

4. The final readings of the Mueller bridge were N = 26.23795 and R = 26.2384 ohms.

The following procedure was used to calculate the heat capacity:

The resistance of the thermometer = $(N + R)/2$.

The temperature corresponding to the resistance of the thermometer was calculated using the method of successive iteration (see Appendix F) from the Callendar-van Dusen equation with constants given by the National Bureau of Standards for this thermometer. The Callendar-van Dusen equation was first approximated with a fourth degree polynomial using resistance as the independent variable. This polynomial provided an initial

trial temperature, t_1, for the successive iteration which was carried out as follows

$$t_2 = f(t_1)$$
$$t_3 = f(t_2)$$
$$\cdots\cdots\cdots$$
$$t_n = f(t_{n-1})$$

where $t = f(t)$ was the Callendar-van Dusen equation which satisfied the condition of convergence for the successive iteration method. The iteration was stopped when $|t_n - t_{n-1}| < 0.0001$. For the temperature range of this research, this method could obtain a temperature within 0.0004°C. of the correct temperature.

When such a calculation was carried out on the data reported above, the following results were obtained

initial resistance of the thermometer = 25.8284 ohms

initial temperature = 3.2261°C.

final resistance of the thermometer = 26.238175 ohms

final temperature = 7.2669°C.

midpoint temperature or mean temperature = 5.2465°C.

temperature increment Δt = 4.0408°C.

The potential reading across the heater was reduced by a volt box, which was in parallel with the heater, by a 1 : 200 ratio; therefore the potential across the heater was 200 P. The current measured from the potential, Q, across the one ohm standard resistor partly flowed through

the volt box. After taking this into consideration, the current in the heater was computed to be $(Q/1.00044 - 200P/60000)$, where 1.00044 is the resistance of the standard resistor and 60000 is the resistance across the volt box.

The energy input, H, to the calorimeter can in the heating interval, S, was

$$H = (Q/1.00044 - 200P/60000) \cdot 200P \cdot S/4.1840 \text{ defined calorie.}$$

For the data reported above,

$$H = 65.6748 \text{ calorie.}$$

The apparent heat capacity of the calorimeter can, which was filled with nitrogen gas near room temperature at atmospheric pressure, was 65.6748/4.0408 = 16.253 cal./°C. The heat capacity of the nitrogen gas inside the can was estimated, assuming an ideal gas, to be 0.033 cal./°C.; this value was used in all instances to correct the apparent heat capacity to the true heat capacity of the can.

The heat capacity of the can = 16.253 - 0.033 = 16.220 cal./°C.

The following data are presented in Table 7, Appendix C, for this particular measurement:

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./°C.
3.226	5.246	16.220

Sample Calculation for the Heat Capacity of the Pure Liquid

The following data were obtained for a particular measurement for toluene:

weight of sample		138.54 gm.	
initial resistance reading	N	21.84515	ohm
	R	21.8442	
potential reading	P	0.066693	volt
	Q	0.090145	
heating interval	S	838.0 sec.	
final resistance reading	N	22.2126	ohm
	R	22.2119	

The following data were calculated according to the method outlined above:

initial resistance of the thermometer = 21.844675 ohms

initial temperature = -35.8032°C.

final resistance of the thermometer = 22.21225 ohms

final temperature = -32.2219°C.

mean temperature = -34.0126°C.

temperature increment = 3.5813°C.

heat input H = 240.108 cal.

The heat capacity of the can evaluated from the polynomial given in Table 13, Appendix C, at -34.0126°C. is 15.630 cal./°C. The number of moles of toluene in the can was 138.5429/92.134 = 1.5037 gm.moles. The heat capacity of toluene, C_p, is computed to be

$$C_p = (240.108 - 15.630 \times 3.5813)/(3.5813 \times 1.5037)$$

$$= 34.192 \text{ cal./gm.mole°C.}$$

The following data are presented in Table 8, Appendix C, for this particular measurement:

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole°C.
-35.803	-34.012	34.192

The unfilled space in the calorimeter can was kept at about 10 ml. near room temperature when the can was sealed. The unfilled space contained nitrogen gas and the vapor from the liquid (see also Chapter IV). The heat capacity of the gas in the vapor space was estimated to be less than 0.006 cal./°C. and therefore was neglected in all the calculations for liquid samples.

The heat effect due to evaporation of the liquid sample of each measurement was estimated as follows: The ethanol has the highest vapor pressure and heat of vaporization among the three pure substances near 35°C. Its vapor pressure, estimated from the value given by A. P. I.[30] at 30°C. is 80 mm. Hg. and at 35°C. is 105 mm Hg. The heat of vaporization in this temperature range was estimated to be 10503 cal./gm.mole from the vapor pressure equation and the Clausius-Clapeyron relation. Assuming ideal gas, the number of moles of ethanol vapor in the can at 30°C. is

$$(80/760) \cdot (10/82.06 \times 303) = 4.2 \times 10^{-5} \text{ gm. mole}$$

at 35°C. is

$$(105/760) \cdot (10/82.06 \times 308) = 5.4 \times 10^{-5} \text{ gm. mole.}$$

Therefore, the heat of vaporization of this measurement is

$$(5.4 \times 10^{-5} - 4.2 \times 10^{-5}) \times 10503 = 0.13 \text{ cal.}$$

or an error of approximately

$$0.13/5 \times 1.7 = 0.015 \text{ cal./gm.mole } ^\circ\text{C.}$$

in the heat capacity data. This error diminishes rapidly with lowering of temperature. Therefore this effect was neglected in computing the heat capacity data of both pure liquids and mixtures.

Sample Calculation for Heat Capacity of Solutions

The following data were obtained for a particular measurement of the ethanol-toluene system:

sample weight	138.98 grams		
weight fraction of ethanol in sample	0.0325		
initial resistance reading	N	19.3629	ohms
	R	19.3628	
potential reading	P	0.067599	volt
	Q	0.091447	
final resistance reading	N	19.7808	ohms
	R	19.78115	

The total number of moles in the sample is

$$n = n_a + n_h = 138.98 \times 0.0325/92.134 + 138.98 \times 0.9675/46.068$$

$$= 2.9677 \text{ gm. moles}$$

According to the procedure outlined above, the following data were obtained:

initial temperature -59.8694°C.

mean temperature -57.8494°C.

heat capacity of the solution 33.124 cal./gm.mole°C.

The heat capacity of ethanol and toluene at -57.8494°C, computed from the polynomials given in Table 13, Appendix C, is 21.924 and 33.196, respectively.

The excess heat capacity, C_p^E, is

$$C_p^E = 33.124 - (21.92n_a + 33.19n_h)$$

$$= 0.636 \text{ cal./gm.mole°C.}$$

The following data are presented in Table 12, Appendix C, for this measurement.

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole°C.	Excess Heat Capacity cal./gm.mole°C.
-59.869	-57.849	33.124	0.636

APPENDIX C

HEAT CAPACITY DATA

Table 7. Heat Capacity of the Calorimeter Can

(Can Weight 193.60 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity Cal./°C.
22.772*	24.488	16.484
26.186	28.041	16.558
22.287	24.566	16.512
29.775	31.302	16.613
26.649	28.160	16.541
29.660	31.365	16.613
0.110	1.668	16.182
3.226**	5.246	16.220
7.266	8.919	16.281
10.572	12.021	16.323
13.470	14.953	16.353
-116.990	-115.363	13.809
-113.737	-111.948	13.920
-110.159	-108.526	14.038
-106.894	-105.328	14.131
-103.761	-102.126	14.220
-82.613	-80.736	14.753
-78.858	-76.521	14.860
-74.183	-73.009	14.922
-71.835	-69.499	15.009
-67.163	-65.897	15.074
-64.631	-62.304	15.143
-59.978	-57.599	15.236
-55.220	-53.601	15.303
-101.409	-99.003	14.309
-96.598	-94.346	14.433
-92.094	-89.984	14.543
-87.874	-85.781	14.645
-56.260	-54.631	15.280
-53.003	-50.895	15.356
-48.788	-46.549	15.427
-44.309	-42.195	15.495
-40.080	-38.013	15.571
-35.945	-33.911	15.640
-31.877	-29.786	15.705
-27.701	-25.658	15.760

*The data listed for each sample are arranged in chronological order.

** Data used in sample calculation.

Table 7 - Continued

(Can Weight 193.60 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity Cal./°C.
-26.647	-24.637	15.784
-22.626	-20.640	15.857
-18.653	-16.640	15.919
-10.669	-8.535	16.020
-6.405	-4.240	16.073
-2.081	0.115	16.175
-127.070	-125.341	13.446
-123.613	-121.812	13.581
-120.011	-118.203	13.714
-116.395	-114.634	13.838

Table 8. Heat Capacity of Toluene

(Sample Weight 138.54 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.
21.748	22.913	37.446
24.080	25.561	37.603
27.041	28.413	37.805
29.785	31.297	37.975
12.282	13.740	36.793
15.198	16.671	36.982
18.143	19.755	37.199
0.840	2.535	36.088
4.230	5.945	36.302
7.661	9.354	36.544
11.047	12.645	36.748
1.718	3.105	36.115
4.493	6.144	36.309
-93.518	-92.259	32.374
-90.999	-89.459	32.414
-87.919	-86.401	32.458
-84.882	-83.329	32.530
-73.479	-71.885	32.764
-70.291	-68.582	32.851
-66.872	-65.104	32.954
-63.335	-61.542	33.063
-59.750	-57.910	33.180
-56.069	-54.230	33.314
-52.391	-50.553	33.456
-39.291	-37.547	34.011
-35.803*	-34.012	34.192
-32.221	-30.454	34.383
-28.687	-26.957	34.573
-25.226	-23.347	34.733
-21.472	-19.972	34.893
-15.452	-13.771	35.251
-12.091	-10.397	35.427
-8.703	-6.987	35.581
-5.271	-3.584	35.752

*Data used in sample calculation.

Table 9. Heat Capacity of Methylcyclohexane

(Sample Weight 118.68 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.
0.118	1.684	41.956
3.250	5.045	42.272
6.839	8.866	42.624
10.892	12.898	43.052
14.850	16.841	43.383
18.832	20.877	43.793
22.921	24.905	44.281
26.889	28.529	44.552
30.169	31.777	44.968
33.384	34.986	45.325
-99.986	-98.359	34.723
-96.732	-94.690	34.932
-92.648	-90.397	35.228
-88.146	-85.869	35.362
-83.592	-81.170	35.732
-78.749	-76.568	35.888
-75.271	-73.291	36.145
-71.312	-68.955	36.426
-66.598	-64.243	36.714
-61.887	-59.550	37.041
-57.212	-55.393	37.321
-54.120	-51.845	37.575
-49.570	-47.300	37.885
-45.031	-42.790	38.227
-40.550	-38.337	38.568
-36.124	-33.904	38.914
-31.684	-29.244	39.294
-26.804	-24.362	39.690
-21.911	-19.506	40.100
-17.100	-14.701	40.493
-12.301	-9.942	40.914
-7.582	-5.308	41.317

Table 10. Heat Capacity of Ethanol

(Sample Weight 112.99 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.
-109.384	-107.839	21.016
-106.294	-104.613	21.039
-102.933	-101.302	21.072
-99.672	-98.110	21.104
-94.924	-93.293	21.160
-91.661	-90.041	21.206
-88.421	-86.785	21.257
-85.149	-83.526	21.309
-81.902	-80.342	21.372
-78.781	-77.181	21.434
-69.841	-68.218	21.636
-66.595	-65.087	21.712
-63.579	-61.969	21.792
-60.359	-58.792	21.889
-57.224	-55.654	21.985
-54.084	-52.561	22.080
-46.194	-44.574	22.367
-42.953	-41.342	22.510
-39.730	-38.099	22.636
-36.468	-34.860	22.783
-33.251	-31.560	22.935
-29.901	-28.412	23.075
-26.922	-25.394	23.232
-23.865	-22.260	23.390
-20.655	-19.173	23.564
-17.692	-16.143	23.730
-14.595	-13.087	23.908
-11.578	-9.789	24.113
-7.999	-6.187	24.341
-4.375	-2.527	24.604
-0.679	1.122	24.867
2.306	3.966	25.049
5.626	7.407	25.326
9.188	10.876	25.601
12.564	14.213	25.873
15.863	17.572	26.174
19.281	20.925	26.462
22.570	24.209	26.782
22.070	23.998	26.752
25.927	27.937	27.145
29.948	31.054	27.473

Table 11. Heat Capacity of Ethanol-Methylcyclohexane System

Mixture Composition 0.0742 Mole Fraction Ethanol

(Sample Weight 116.53 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
0.315	2.843	42.060	1.261
5.371	7.722	42.698	1.444
10.073	12.496	43.321	1.610
14.920	17.401	43.977	1.787
20.218	22.736	44.700	1.976
25.254	27.251	45.319	2.132
29.248	30.816	45.866	2.307
32.383	33.950	46.313	2.422
-62.943	-60.584	35.981	0.133
-58.226	-56.026	36.311	0.165
-53.827	-51.255	36.667	0.201
-48.684	-46.118	37.091	0.269
-40.767	-38.198	37.723	0.330
-35.630	-32.988	38.219	0.434
-30.292	-27.801	38.700	0.514
-25.310	-22.700	39.198	0.607
-20.090	-17.397	39.751	0.725
-14.705	-12.034	40.336	0.858
-9.363	-6.686	40.933	0.992

Table 11 - Continued

Mixture Composition 0.1979 Mole Fraction Ethanol

(Sample Weight 118.97 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
0.234	2.233	40.119	1.488
4.231	6.822	40.720	1.673
9.412	11.942	41.431	1.907
14.472	16.983	42.143	2.136
19.298	21.773	42.843	2.364
24.249	26.744	43.608	2.625
29.240	30.539	44.269	2.893
31.838	33.125	44.658	3.009
-67.488	-65.189	33.804	0.097
-62.891	-60.385	34.114	0.126
-57.879	-55.399	34.453	0.162
-52.919	-50.454	34.826	0.224
-47.990	-45.592	35.195	0.275
-36.893	-34.555	36.112	0.433
-32.217	-29.786	36.575	0.551
-27.356	-24.886	37.034	0.644
-22.415	-19.980	37.542	0.773
-15.776	-13.288	38.250	0.946
-10.799	-8.094	38.853	1.119
-5.389	-2.862	39.495	1.314

Table 11 - Continued

Mixture Composition 0.3456 Mole Fraction Ethanol

(Sample Weight 121.19 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
-69.808	-67.599	31.487	0.113
-65.390	-62.939	31.737	0.122
-60.488	-58.014	32.033	0.152
-55.539	-53.048	32.337	0.176
-50.558	-47.973	32.685	0.227
-45.387	-42.741	33.070	0.292
-40.094	-37.407	33.494	0.376
-34.719	-31.899	33.950	0.467
-29.079	-26.335	34.461	0.593
-23.646	-20.902	34.985	0.725
-18.157	-15.466	35.533	0.865
-12.774	-10.110	36.107	1.023
-7.446	-4.822	36.713	1.201
1.370	3.955	37.801	1.544
6.461	9.052	38.481	1.770
11.644	14.148	39.208	2.028
16.651	19.101	39.923	2.270
21.552	23.978	40.664	2.532
26.403	28.773	41.436	2.816
27.991	29.525	41.531	2.833
31.059	32.357	42.003	3.009
33.655	34.718	42.391	3.145

Table 11 - Continued

Mixture Composition 0.5324 Mole Fraction Ethanol

(Sample Weight 118.58 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
0.662	2.655	34.142	1.189
4.649	7.003	34.673	1.353
9.357	11.722	35.285	1.551
14.061	16.412	35.920	1.759
18.763	21.059	36.533	1.932
23.354	25.726	37.254	2.194
28.099	29.915	37.909	2.424
31.731	33.340	38.462	2.617
-68.680	-66.480	28.660	0.013
-74.279	-61.933	28.882	0.030
-59.587	-57.223	29.118	0.043
-54.860	-52.457	29.388	0.077
-47.495	-45.024	29.834	0.132
-45.376	-43.122	29.961	0.153
-40.867	-38.427	30.289	0.214
-35.986	-33.529	30.658	0.292
-31.211	-28.818	31.015	0.357
-26.425	-23.955	31.431	0.458
-21.485	-19.024	31.873	0.566
-16.564	-14.244	32.320	0.676
-11.924	-9.407	32.814	0.814
-6.891	-4.315	33.334	0.944

Table 11 - Continued

Mixture Composition 0.8004 Mole Fraction Ethanol

(Sample Weight 118.50 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
0.226	2.390	28.865	0.513
4.555	6.940	29.318	0.604
9.325	11.708	29.820	0.709
14.091	16.426	30.331	0.808
18.762	21.018	30.856	0.911
23.273	25.539	31.435	1.056
27.640	29.223	31.896	1.147
30.806	32.379	32.334	1.259
-68.091	-65.984	24.555	-0.113
-63.876	-61.766	24.709	-0.106
-59.655	-57.067	24.904	-0.086
-54.478	-52.165	25.117	-0.068
-49.853	-47.449	25.335	-0.050
-45.045	-42.512	25.587	-0.021
-39.980	-37.188	25.881	0.017
-29.380	-26.843	26.524	0.113
-24.305	-21.729	26.879	0.172
-19.153	-16.553	27.244	0.220
-13.953	-11.455	27.660	0.305
-8.957	-6.483	28.057	0.361

Table 12. Heat Capacity of Ethanol-Toluene System

Mixture Composition 0.0630 Mole Fraction Ethanol

(Sample Weight 138.98 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
-59.869*	-57.849	33.124	0.636
-55.829	-53.553	33.337	0.690
-51.278	-49.126	33.579	0.756
-46.973	-44.846	33.825	0.825
-42.719	-40.598	34.092	0.908
-38.476	-36.317	34.352	0.975
-34.158	-32.119	34.639	1.066
-28.133	-26.074	35.033	1.168
-24.016	-21.675	35.353	1.267
-19.334	-17.046	35.684	1.359
-14.757	-12.385	36.010	1.438
-10.012	-7.746	36.357	1.531
0.173	2.091	37.046	1.656
4.008	6.352	37.340	1.694
8.696	10.900	37.658	1.729
13.105	15.251	37.945	1.736
17.528	19.549	38.183	1.686
21.569	23.777	38.455	1.665
25.985	28.166	38.617	1.510
20.506	22.265	38.351	1.667
24.025	25.897	38.567	1.626
27.769	29.417	38.637	1.437
-94.909	-92.729	31.922	0.236
-90.549	-88.475	32.017	0.295
-86.401	-84.249	32.118	0.340
-82.096	-79.883	32.244	0.388
-77.670	-75.576	32.381	0.431
-73.483	-71.342	32.529	0.471
-69.201	-67.148	32.713	0.535
-65.095	-63.051	32.878	0.571

*Data used in sample calculation.

Table 12 - Continued

Mixture Composition 0.0969 Mole Fraction Ethanol

(Sample Weight 136.88 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
0.551	2.234	37.059	2.038
3.918	5.957	37.379	2.133
7.996	10.043	37.682	2.180
12.091	14.140	37.996	2.230
16.189	18.282	38.317	2.274
20.437	22.472	38.627	2.293
24.507	26.512	38.934	2.308
28.516	30.517	39.234	2.307
32.518	34.323	39.501	2.276
-95.437	-93.457	31.579	0.278
-91.478	-89.203	31.673	0.337
-86.928	-84.737	31.786	0.393
-82.546	-80.313	31.929	0.460
-78.080	-76.195	32.042	0.485
-74.325	-72.189	32.211	0.555
-70.052	-67.827	32.374	0.596
-65.601	-63.488	32.580	0.667
-61.375	-59.295	32.767	0.713
-57.215	-55.362	32.970	0.773
-49.843	-47.740	33.388	0.892
-45.637	-43.612	33.638	0.969
-41.587	-39.702	33.904	1.064
-36.889	-34.811	34.230	1.169
-32.733	-30.761	34.512	1.260
-28.790	-26.787	34.810	1.365
-24.784	-22.814	35.107	1.464
-20.844	-18.899	35.404	1.560
-16.953	-14.850	35.716	1.660
-12.747	-10.429	36.054	1.759
-7.831	-5.607	36.447	1.884
-3.383	-1.731	36.789	2.003
0.277	2.297	37.081	2.057
4.317	6.359	37.403	2.132
8.402	10.594	37.735	2.199
12.787	14.981	38.073	2.252

Table 12 - Continued

Mixture Composition 0.1841 Mole Fraction Ethanol

(Sample Weight 135.07 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
-94.835	-93.017	30.710	0.386
-91.199	-89.064	30.797	0.437
-86.929	-84.741	30.917	0.501
-82.581	-80.676	31.030	0.544
-78.771	-76.889	31.164	0.599
-75.007	-72.765	31.319	0.655
-70.524	-68.287	31.505	0.719
-64.123	-62.087	31.795	0.817
-60.050	-57.993	32.021	0.904
-52.249	-50.253	32.444	1.037
-48.258	-46.127	32.704	1.132
-43.997	-41.943	32.980	1.231
-39.888	-37.767	33.286	1.352
-34.741	-32.524	33.669	1.494
-30.307	-27.957	34.024	1.630
-25.516	-23.149	34.420	1.787
-20.781	-18.410	34.827	1.950
-16.116	-13.923	35.204	2.088
-11.730	-9.467	35.613	2.251
-7.203	-4.973	36.018	2.401
-0.069	1.778	36.593	2.575
3.627	5.825	36.965	2.697
8.024	10.180	37.395	2.848
12.336	14.495	37.797	2.962
16.654	18.823	38.208	3.075
20.641	22.742	38.543	3.129
24.842	27.033	38.955	3.214
29.224	31.267	39.356	3.290
33.310	35.347	39.742	3.342

Table 12 - Continued

Mixture Composition 0.2748 Mole Fraction Ethanol

(Sample Weight 131.96 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
-51.988	-50.303	31.474	1.097
-48.618	-46.822	31.697	1.181
-93.561	-92.049	29.732	0.417
-90.537	-88.677	29.819	0.471
-86.817	-84.761	29.933	0.532
-82.706	-80.768	30.042	0.572
-78.849	-76.925	30.172	0.623
-75.001	-73.028	30.326	0.685
-71.054	-69.092	30.484	0.738
-67.130	-65.049	30.667	0.803
-62.339	-60.255	30.912	0.894
-58.171	-55.908	31.141	0.973
-53.646	-52.148	31.362	1.055
-49.246	-47.416	31.664	1.172
-45.585	-43.420	31.926	1.269
-41.255	-39.195	32.235	1.396
-37.134	-35.111	32.531	1.509
-33.088	-31.121	32.843	1.635
-29.155	-27.147	33.171	1.771
-25.139	-23.174	33.489	1.890
-21.208	-19.172	33.839	2.033
-17.136	-15.191	34.185	2.166
-12.404	-10.489	34.613	2.335
-8.573	-6.623	34.988	2.491
-4.773	-2.826	35.345	2.621
-0.878	1.086	35.754	2.793
1.147	2.238	35.847	2.813
3.329	5.285	36.157	2.931
7.241	9.206	36.559	3.077
10.871	12.933	36.936	3.203
14.994	17.062	37.368	3.345
19.131	21.173	37.799	3.477
23.216	25.266	38.227	3.594
27.316	29.195	38.654	3.711

Table 12 - Continued

Mixture Composition 0.4505 Mole Fraction Ethanol

(Sample Weight 131.90 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
-95.428	-93.731	27.750	0.423
-92.034	-89.900	27.838	0.473
-87.766	-85.715	27.916	0.495
-83.664	-81.569	28.044	0.554
-79.474	-77.277	28.166	0.591
-75.081	-72.966	28.320	0.645
-70.852	-68.589	28.492	0.704
-66.326	-64.043	28.694	0.776
-61.759	-59.505	28.908	0.846
-50.369	-48.419	29.529	1.069
-46.468	-44.438	29.783	1.165
-42.459	-40.226	30.071	1.276
-38.042	-35.903	30.367	1.382
-33.764	-31.623	30.719	1.536
-29.481	-27.360	31.053	1.665
-25.239	-23.116	31.402	1.801
-32.677	-30.872	30.745	1.527
-29.066	-27.173	31.061	1.664
-25.279	-23.338	31.374	1.784
-21.398	-19.447	31.725	1.933
-17.497	-15.611	32.072	2.071
-13.724	-11.832	32.418	2.206
-9.940	-8.139	32.766	2.340
0.018	1.802	33.763	2.721
3.585	5.658	34.174	2.878
7.731	10.059	34.653	3.054
12.387	14.433	35.127	3.214
16.480	18.668	35.608	3.377
20.358	22.335	36.014	3.496
24.312	26.261	36.475	3.638
28.210	29.496	36.873	3.764

Table 12 - Continued

Mixture Composition 0.6439 Mole Fraction Ethanol

(Sample Weight 130.76 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
-90.959	-89.767	25.577	0.378
-88.575	-86.566	25.650	0.407
-84.558	-82.496	25.738	0.428
-80.435	-78.388	25.840	0.452
-76.341	-74.242	25.964	0.485
-72.139	-70.088	26.099	0.519
-68.037	-65.910	26.251	0.559
-63.783	-61.724	26.418	0.604
-59.664	-57.621	26.601	0.657
-50.588	-48.448	27.069	0.801
-46.307	-44.264	27.303	0.873
-42.221	-40.218	27.554	0.957
-38.209	-36.259	27.809	1.041
-34.310	-32.392	28.074	1.130
-30.474	-28.564	28.346	1.220
-26.655	-24.757	28.637	1.321
-22.860	-20.821	28.957	1.437
-18.783	-16.850	29.285	1.550
-14.917	-12.909	29.609	1.650
-10.900	-8.885	29.972	1.776
-6.870	-5.732	30.282	1.892
0.397	2.412	31.063	2.141
4.428	6.527	31.486	2.278
8.625	10.709	31.934	2.421
12.705	14.740	32.403	2.583
16.775	18.865	32.827	2.679
20.956	23.043	33.322	2.826
25.129	27.074	33.830	2.983

Table 12 - Continued

Mixture Composition 0.8026 Mole Fraction Ethanol

(Sample Weight 123.39 gm.)

Initial Temp. °C.	Mean Temp. °C.	Heat Capacity cal./gm.mole °C.	Excess Heat Capacity cal./gm.mole °C.
1.779	3.206	28.539	1.332
4.634	6.371	28.837	1.401
8.108	9.807	29.176	1.481
11.506	13.225	29.517	1.554
14.945	16.770	29.901	1.649
19.786	21.245	30.380	1.747
22.703	24.540	30.744	1.817
26.377	27.801	31.154	1.926
29.224	30.658	31.459	1.958
32.091	33.521	31.841	2.058
34.950	36.351	32.195	2.123
-94.927	-93.204	23.619	0.241
-91.482	-89.493	23.681	0.257
-87.505	-85.450	23.750	0.265
-83.395	-81.285	23.834	0.276
-79.174	-76.774	23.937	0.290
-73.412	-71.347	24.079	0.309
-69.282	-67.000	24.211	0.331
-64.718	-62.710	24.357	0.358
-60.701	-57.797	24.545	0.396
-49.897	-48.178	24.955	0.475
-46.459	-44.738	25.121	0.510
-43.017	-40.835	25.330	0.562
-38.652	-36.420	25.567	0.611
-34.189	-31.874	25.856	0.694
-29.819	-27.979	26.087	0.739
-26.140	-24.234	26.339	0.803
-22.329	-20.272	26.611	0.867
-18.216	-16.155	26.915	0.942
-14.095	-12.046	27.243	1.031
-9.998	-7.981	27.564	1.105

Table 13. List of Polynomials Representing the Heat Capacity Data

The polynomial,

$$C_p = b_1 + b_2 t + b_3 t^2 + b_4 t^3 + b_5 t^4$$

is used to represent the experimental data given in Tables 7,8,9, and 10.

	Calorimeter Can	Toluene	Methylcyclohexane	Ethanol
b_1	16.150851	35.973061	41.803227	24.771365
b_2	1.4611653×10^{-2}	5.7538545×10^{-2}	9.2460288×10^{-2}	7.1335467×10^{-2}
b_3	$-9.8269990 \times 10^{-6}$	1.8395320×10^{-4}	2.0971222×10^{-4}	4.4869668×10^{-4}
b_4	1.1551778×10^{-7}	1.2063987×10^{-6}	0	1.3279642×10^{-6}
b_5	$-1.9636810 \times 10^{-9}$	1.5372579×10^{-8}	0	2.8672268×10^{-9}

The polynomial,

$$C_p^E = b_1 + b_2 T + b_3 T^2 + \cdots + b_n T^{n-1}$$

is used to represent the excess heat capacity data of the mixtures given in Tables 11 and 12.

	Ethanol-Methylcyclohexane System			
x_a*	0.0742	0.1979	0.3456	0.5324
b_1	8.3731960	1.5405540	6.1399340	3.4812000×10^{-2}
b_2	$-8.2408440 \times 10^{-2}$	8.2916200×10^{-3}	$-4.0858420 \times 10^{-2}$	3.0026290×10^{-2}
b_3	2.0538945×10^{-4}	$-2.0414560 \times 10^{-4}$	$-3.4359210 \times 10^{-5}$	$-3.0160674 \times 10^{-4}$
b_4	0	6.2952841×10^{-7}	4.4057809×10^{-7}	7.5394132×10^{-7}

*Composition of the mixture in mole fraction ethanol.

Table 13 - Continued

	Ethanol-Methylcyclohexane System
x_a	0.8004
b_1	-3.8398670
b_2	5.9174350×10^{-2}
b_3	$-3.2479908 \times 10^{-4}$
b_4	6.0759421×10^{-7}

	Ethanol-Toluene System			
x_a	0.0630	0.0969	0.1841	0.2748
b_1	31.011770	-56.636237	-43.766837	-43.039022
b_2	-0.94121920	1.0435962	0.82437420	0.80480220
b_3	1.0658179×10^{-2}	$-7.1890101 \times 10^{-3}$	$-5.7841820 \times 10^{-3}$	$-5.5990414 \times 10^{-3}$
b_4	$-5.7794746 \times 10^{-5}$	2.1899427×10^{-5}	1.7865288×10^{-5}	1.7118192×10^{-5}
b_5	1.5232745×10^{-7}	$-2.4493676 \times 10^{-8}$	$-2.0012871 \times 10^{-8}$	$-1.8893341 \times 10^{-8}$
b_6	$-1.5626273 \times 10^{-10}$	0	0	0

x_a	0.4505	0.6439	0.8026
b_1	-35.184545	-20.924237	6.7896583
b_2	0.67294294	0.41675678	$-7.8357805 \times 10^{-2}$
b_3	$-4.7490739 \times 10^{-3}$	$-3.0143057 \times 10^{-3}$	2.7468441×10^{-4}
b_4	1.4616270×10^{-5}	9.3850002×10^{-6}	$-2.2666805 \times 10^{-7}$
b_5	$-1.6081074 \times 10^{-8}$	$-1.0277498 \times 10^{-8}$	0

Table 14. Comparison of Heat Capacity of Toluene

Temp. °C.	A* cal./gm.mole °C.	B** cal./gm.mole °C.	A - B cal./gm.mole °C.
30.0	37.909	37.924	-0.015
25.0	37.551	37.582	-0.031
20.0	37.209	37.246	-0.037
15.0	36.882	36.917	-0.034
10.0	36.568	36.594	-0.026
5.0	36.265	36.279	-0.014
0.0	35.973	35.973	-0.000
-5.0	35.689	35.675	0.014
-10.0	35.415	35.386	0.028
-15.0	35.148	35.107	0.040
-20.0	34.888	34.838	0.050
-25.0	34.636	34.580	0.056
-30.0	34.392	34.334	0.058
-35.0	34.155	34.099	0.056
-40.0	33.927	33.876	0.051
-45.0	33.709	33.667	0.041
-50.0	33.501	33.471	0.029
-55.0	33.304	33.289	0.015
-60.0	33.121	33.122	-0.000
-65.0	32.953	32.969	-0.016
-70.0	32.802	32.833	-0.031
-75.0	32.669	32.712	-0.042
-80.0	32.559	32.608	-0.049
-85.0	32.472	32.522	-0.049
-90.0	32.413	32.453	-0.039
-95.0	32.384	32.402	-0.017
-100.0	32.389	32.370	0.018

*Heat capacity of the present work, calculated from the polynomial given in Table 13, Appendix C.

**Heat capacity measured by Scott *et al.*[33], calculated from the polynomial given by them.

Table 15. Comparison of Heat Capacity of Methylcyclohexane

Temp. °C.	A* cal./gm.mole °C.	B** cal./gm.mole °C.	A - B cal./gm.mole °C.
12.610	43.002	42.936	0.066
-0.480	41.758	41.750	0.008
-13.930	40.555	40.554	0.001
-26.870	39.470	39.469	0.001
-39.250	38.497	38.474	0.023
-51.940	37.566	37.520	0.046
-63.990	36.745	36.681	0.064
-75.350	36.027	36.010	0.017
-86.950	35.349	35.347	0.002
-82.410	35.049	35.032	0.017
-97.780	34.767	34.778	-0.010
-102.390	34.534	34.521	0.013

*Heat capacity of the present work, calculated from the polynomial given in Table 13, Appendix C.

**Experimental heat capacity data points reported by Douslin and Huffman[34].

APPENDIX D

PRESSURE EFFECT ON EXCESS THERMODYNAMIC PROPERTIES

The pressure effect on the excess thermodynamic excess properties of solutions at constant temperature and composition may be expressed in the following relations:

$$\left[\frac{\partial G^E}{\partial P} = V^E\right]_{T,x} \tag{45}$$

$$\left[\left(\frac{\partial H^E}{\partial P}\right)_T = V^E - T\left(\frac{\partial V^E}{\partial T}\right)_P\right]_x \tag{46}$$

$$\left[\left(\frac{\partial S^E}{\partial P}\right)_T = -\left(\frac{\partial V^E}{\partial T}\right)_P\right]_x \tag{47}$$

$$\left[\left(\frac{\partial C_P^E}{\partial P}\right)_T = -T\left(\frac{\partial^2 V^E}{\partial T^2}\right)_P\right]_x \tag{48}$$

The neglect of the pressure effect can introduce into the excess properties an error of the following magnitude:

$$\Delta G^E = \int_{P_1}^{P_2} V^E \, dP \tag{49}$$

$$\Delta H^E = \int_{P_1}^{P_2} \left[V^E - T\left(\frac{\partial V^E}{\partial T}\right)_P\right] dP \tag{50}$$

$$\Delta S^E = \int_{P_1}^{P_2} -\left(\frac{\partial V^E}{\partial T}\right)_P dP \tag{51}$$

$$\Delta C_P^E = \int_{P_1}^{P_2} -T\left(\frac{\partial^2 V^E}{\partial T^2}\right)_P dP \qquad (52)$$

Below one atmospheric pressure, the maximum error will occur when $P_1 = 0$ and $P_2 = 1$ atm. If the excess volume of mixing were known as a function of temperature near atmospheric pressure, the maximum errors could be calculated from Equations (49), (50), (51), and (52). However, for the ethanol-methylcyclohexane system and the ethanol-toluene system, the only reliable excess volume of mixing data available are those isothermal measurements of Kretschmer and Wiebe[36,37] and Washburn and Lightbody[52] at 25°C. The maximum value of V^E of the ethanol-methylcyclohexane system at 25°C. is 0.0056 ml./gm., of the ethanol-toluene system is -0.0019 ml./gm. From Equation (49), for the ethanol-methylcyclohexane system,

$$\Delta G^E \cong \int_0^1 0.0056 \times \frac{100}{1000}\, dP \quad \text{liter-atm./gm.mole}$$

$$= 0.00056 \quad \text{liter-atm./gm.mole}$$

$$= 0.014 \text{ cal./gm. mole}$$

for the ethanol-toluene system,

$$\Delta G^E \cong \int_0^1 -0.0019 \times \frac{100}{1000}\, dP \quad \text{liter-atm./gm.mole}$$

$$= -0.00019 \quad \text{liter-atm./gm.mole}$$

$$= -0.005 \text{ cal./gm.mole}$$

Therefore, the pressure effect is negligible to the excess free energy in this region.

Since the temperature dependence of V^E of these two systems is not available, the V^E of the ethanol-2,2,4-trimethylpentane system, which has nonideal behavior very similar to that of the ethanol-methylcyclohexane system, measured at 0° and 50°C. by Kretschmer[53], et al., were used to estimate the quantity $\left(\frac{\partial V^E}{\partial T}\right)_P$. The estimated maximum value of $\left(\frac{\partial V^E}{\partial T}\right)_P$ is about 3×10^{-6} liter/gm.mole°K. ΔH^E is estimated from Equation (50) to be less than 0.05 cal./gm.mole, and ΔS^E is estimated from Equation (51) to be less than 0.0002 e.u.

These calculations indicate that the pressure effect on the excess thermodynamic properties is considerably smaller than the uncertainty in the value of excess properties itself. Therefore, for the pressure range involved in this work, the pressure effect on the excess thermodynamic properties of these two systems, ethanol-methylcyclohexane and ethanol-toluene, can be neglected without affecting the accuracy of the data.

APPENDIX E

DERIVED THERMODYNAMIC PROPERTIES AND ACTIVITY COEFFICIENTS

Table 16. Derived Excess Thermodynamic Properties of Ethanol-Methycyclohexane System

x_a	0.0742	0.1979	0.3456	0.5324	0.8004
T°K.	Excess Enthalpy cal./gm. mole				
308.15	108.2	149.4	160.2	153.2	95.4
303.15	96.3	134.5	145.0	140.4	89.1
298.15	85.5	121.0	131.4	129.0	83.6
293.15	75.7	108.9	119.2	118.8	78.7
288.15	66.8	98.1	108.3	109.8	74.5
283.15	58.9	88.5	98.6	101.9	70.9
278.15	51.7	80.0	90.1	95.1	67.9
273.15	45.4	72.5	82.6	89.1	65.3
268.15	39.8	65.9	76.1	84.1	63.1
263.15	35.0	60.2	70.5	79.8	61.4
258.15	30.7	55.3	65.7	76.1	60.0
253.15	27.1	51.1	61.7	73.2	58.9
248.15	24.0	47.6	58.3	70.7	58.1
243.15	21.3	44.6	55.5	68.8	57.6
238.15	19.2	42.2	53.2	67.3	57.3
233.15	17.4	40.2	51.3	66.1	57.2
228.15	15.9	38.6	49.9	65.3	57.3
223.15	14.7	37.4	48.7	64.7	57.5
218.15	13.8	36.4	47.8	64.4	57.9
213.15	13.0	35.6	47.0	64.1	58.3
208.15*	12.4	35.1	46.4	64.0	58.9
203.15	11.8	34.6	45.8	63.9	59.5
198.15	11.3	34.3	45.2	63.9	60.1
193.15	10.7	34.0	44.5	63.9	60.9
188.15	10.1	33.6	43.8	63.7	61.6

*Values given below this temperature were obtained by extrapolation.

Table 16 - Continued

x_a	0.0742	0.1979	0.3456	0.5324	0.8004
T°K.	Excess Entropy e.u.				
308.15	-0.0707	-0.3193	-0.5164	-0.5782	-0.3923
303.15	-0.1095	-0.3680	-0.5658	-0.6202	-0.4128
298.15	-0.1454	-0.4127	-0.6111	-0.6583	-0.4312
293.15	-0.1786	-0.4536	-0.6524	-0.6926	-0.4475
288.15	-0.2091	-0.4908	-0.6899	-0.7235	-0.4620
283.15	-0.2370	-0.5245	-0.7238	-0.7511	-0.4746
278.15	-0.2623	-0.5549	-0.7542	-0.7756	-0.4856
273.15	-0.2853	-0.5821	-0.7813	-0.7971	-0.4950
268.15	-0.3059	-0.6063	-0.8053	-0.8158	-0.5029
263.15	-0.3242	-0.6277	-0.8264	-0.8320	-0.5095
258.15	-0.3405	-0.6466	-0.8448	-0.8459	-0.5148
253.15	-0.3547	-0.6629	-0.8607	-0.8576	-0.5190
248.15	-0.3671	-0.6770	-0.8742	-0.8672	-0.5221
243.15	-0.3778	-0.6891	-0.8856	-0.8751	-0.5242
238.15	-0.3869	-0.6992	-0.8951	-0.8814	-0.5254
233.15	-0.3945	-0.7076	-0.9030	-0.8862	-0.5258
228.15	-0.4008	-0.7145	-0.9094	-0.8898	-0.5255
223.15	-0.4061	-0.7200	-0.9145	-0.8924	-0.5245
218.15	-0.4104	-0.7244	-0.9187	-0.8941	-0.5229
213.15	-0.4139	-0.7279	-0.9222	-0.8952	-0.5208
208.15*	-0.4170	-0.7305	-0.9252	-0.8957	-0.5183
203.15	-0.4197	-0.7327	-0.9281	-0.8960	-0.5153
198.15	-0.4224	-0.7344	-0.9310	-0.8962	-0.5119
193.15	-0.4253	-0.7361	-0.9343	-0.8965	-0.5082
188.15	-0.4286	-0.7377	-0.9384	-0.8971	-0.5042

*Values given below this temperature were obtained by extrapolation.

Table 16 - Continued

x_a	0.0742	0.1979	0.3456	0.5324	0.8004
T°K.	Excess Free Energy cal./gm. mole				
308.15	130.0	247.7	319.3	331.4	216.3
303.15	129.5	246.0	316.6	328.4	214.3
298.15	128.9	244.1	313.6	325.2	212.1
293.15	128.1	241.9	310.5	321.9	209.9
288.15	127.1	239.5	307.1	318.3	207.7
283.15	126.0	237.0	303.6	314.6	205.3
278.15	124.7	234.3	299.9	310.8	202.9
273.15	123.4	231.5	296.0	306.9	200.5
268.15	121.9	228.5	292.1	302.8	198.0
263.15	120.3	225.4	288.0	298.7	195.4
258.15	118.6	222.2	283.8	294.5	192.9
253.15	116.9	218.9	279.6	290.3	190.3
248.15	115.1	215.6	275.2	286.0	187.7
243.15	113.2	212.2	270.8	281.6	185.1
238.15	111.3	208.7	266.4	277.2	182.5
233.15	109.4	205.2	261.9	272.8	179.8
228.15	107.4	201.6	257.3	268.3	177.2
223.15	105.4	198.0	252.8	263.9	174.6
218.15	103.3	194.4	248.2	259.4	172.0
213.15	101.2	190.8	243.6	254.9	169.3
208.15*	99.2	187.2	239.0	250.5	166.7
203.15	97.1	183.5	234.3	246.0	164.2
198.15	95.0	179.8	229.7	241.5	161.6
193.15	92.9	176.1	225.0	237.0	159.0
188.15	90.7	172.5	220.3	232.5	156.5

*Values given below this temperature were obtained by extrapolation.

Table 17. Derived Excess Thermodynamic Properties of Ethanol-Toluene System

x_a	0.0630	0.0969	0.1841	0.2748	0.4505	0.6439	0.8026
T°K.	Excess Enthalpy cal./gm.mole						
308.15	142.4	179.1	218.8	230.9	222.1	161.0	96.9
303.15	135.6	167.7	202.3	212.0	202.9	145.3	86.8
298.15	127.9	156.2	186.1	193.7	184.5	130.4	77.3
293.15	119.7	144.6	170.4	176.1	166.9	116.3	68.4
288.15	111.1	133.2	155.2	159.3	150.2	103.1	60.1
283.15	102.4	122.1	140.7	143.3	134.5	90.6	52.4
278.15	93.8	111.3	126.8	128.3	119.8	79.0	45.3
273.15	85.4	101.1	113.8	114.1	106.0	68.3	38.8
268.15	77.4	91.3	101.5	100.9	93.2	58.4	32.7
263.15	69.7	82.2	90.0	88.6	81.4	49.3	27.2
258.15	62.5	73.6	79.4	77.3	70.5	40.9	22.1
253.15	55.8	65.7	69.6	66.9	60.5	33.3	17.5
248.15	49.6	58.3	60.6	57.3	51.4	26.4	13.3
243.15	43.9	51.6	52.3	48.6	43.1	20.1	9.5
238.15	38.6	45.5	44.8	40.6	35.7	14.5	6.1
233.15	33.9	39.9	37.9	33.4	28.9	9.4	3.0
228.15	29.5	34.8	31.8	26.9	22.8	4.8	0.3
223.15	25.6	30.3	26.2	21.1	17.3	0.7	-2.1
218.15	22.0	26.1	21.2	15.8	12.4	-2.8	-4.2
213.15	18.8	22.4	16.7	11.1	8.0	-6.2	-6.2
208.15	15.9	19.1	12.6	6.8	4.0	-9.2	-8.0
203.15	13.3	16.1	9.0	3.0	0.4	-11.9	-9.6
198.15	10.9	13.4	5.7	-0.4	-2.8	-14.4	-11.1
193.15	8.9	11.0	2.8	-3.4	-5.7	-16.6	-12.4
188.15	7.1	8.9	0.2	-6.2	-8.4	-18.8	-13.8
183.15	5.6	7.1	-2.0	-8.6	-10.8	-20.8	-15.1
178.15*	4.4	5.6	-4.0	-10.7	-13.0	-22.6	-16.4
173.15	3.4	4.4	-5.7	-12.5	-15.0	-24.4	-17.7
168.15	2.8	3.6	-7.1	-14.0	-16.8	-26.1	-19.2

*Values given below this temperature were obtained by extrapolation.

Table 17 - Continued

x_a	0.0630	0.0969	0.1841	0.2748	0.4505	0.6439	0.8026
T°K.	Excess Entropy e.u.						
308.15	0.1772	0.1755	0.0677	-0.0518	-0.2005	-0.2911	-0.2394
303.15	0.1551	0.1382	0.0138	-0.1137	-0.2633	-0.3425	-0.2726
298.15	0.1295	0.0998	-0.0400	-0.1745	-0.3246	-0.3921	-0.3042
293.15	0.1015	0.0606	-0.0932	-0.2340	-0.3841	-0.4398	-0.3342
288.15	0.0720	0.0214	-0.1454	-0.2919	-0.4414	-0.4855	-0.3627
283.15	0.0416	-0.0175	-0.1963	-0.3477	-0.4964	-0.5290	-0.3896
278.15	0.0109	-0.0558	-0.2456	-0.4014	-0.5490	-0.5702	-0.4149
273.15	-0.0194	-0.0930	-0.2930	-0.4528	-0.5990	-0.6092	-0.4387
268.15	-0.0491	-0.1290	-0.3383	-0.5016	-0.6462	-0.6459	-0.4611
263.15	-0.0779	-0.1634	-0.3814	-0.5478	-0.6907	-0.6802	-0.4820
258.15	-0.1055	-0.1963	-0.4222	-0.5913	-0.7325	-0.7122	-0.5014
253.15	-0.1317	-0.2273	-0.4607	-0.6321	-0.7715	-0.7420	-0.5195
248.15	-0.1565	-0.2566	-0.4967	-0.6703	-0.8078	-0.7696	-0.5362
243.15	-0.1797	-0.2840	-0.5303	-0.7058	-0.8414	-0.7951	-0.5516
238.15	-0.2015	-0.3095	-0.5616	-0.7388	-0.8725	-0.8185	-0.5657
233.15	-0.2218	-0.3332	-0.5905	-0.7693	-0.9012	-0.8401	-0.5787
228.15	-0.2407	-0.3551	-0.6173	-0.7975	-0.9276	-0.8599	-0.5906
223.15	-0.2581	-0.3754	-0.6420	-0.8235	-0.9519	-0.8780	-0.6015
218.15	-0.2743	-0.3941	-0.6647	-0.8474	-0.9742	-0.8947	-0.6114
213.15	-0.2893	-0.4113	-0.6856	-0.8693	-0.9947	-0.9101	-0.6205
208.15	-0.3031	-0.4272	-0.7049	-0.8895	-1.1013	-0.9243	-0.6289
203.15	-0.3158	-0.4418	-0.7226	-0.9081	-1.1031	-0.9375	-0.6367
198.15	-0.3273	-0.4551	-0.7388	-0.9252	-1.1047	-0.9499	-0.6441
193.15	-0.3378	-0.4673	-0.7537	-0.9409	-1.1062	-0.9615	-0.6511
188.15	-0.3471	-0.4783	-0.7674	-0.9553	-1.1076	-0.9727	-0.6581
183.15	-0.3552	-0.4880	-0.7798	-0.9684	-1.1089	-0.9834	-0.6651
178.15*	-0.3620	-0.4963	-0.7909	-0.9801	-1.1101	-0.9938	-0.6723
173.15	-0.3674	-0.5030	-0.8006	-0.9904	-1.1113	-1.1003	-0.6801
168.15	-0.3711	-0.5076	-0.8088	-0.9990	-1.1123	-1.1013	-0.6886

*Values given below this temperature were obtained by extrapolation.

Table 17 - Continued

x_a	0.0630	0.0969	0.1841	0.2748	0.4505	0.6439	0.8026
T°K.	Excess Free Energy cal./gm. mole						
308.15	87.8	125.0	197.9	246.9	283.9	250.8	170.7
303.15	88.6	125.8	198.1	246.5	282.7	249.2	169.4
298.15	89.3	126.4	198.1	245.8	281.3	247.3	168.0
293.15	89.9	126.8	197.7	244.7	279.5	245.3	166.4
288.15	90.3	127.0	197.1	243.4	277.4	243.0	164.6
283.15	90.6	127.0	196.3	241.8	275.1	240.4	162.8
278.15	90.7	126.9	195.2	240.0	272.5	237.7	160.8
273.15	90.7	126.5	193.8	237.8	269.6	234.7	158.6
268.15	90.5	125.9	192.2	235.4	266.5	231.6	156.4
263.15	90.2	125.2	190.4	232.8	263.1	228.3	154.0
258.15	89.8	124.3	188.4	230.0	259.6	224.8	151.6
253.15	89.2	123.2	186.2	226.9	255.8	221.1	149.0
248.15	88.4	122.0	183.8	223.6	251.9	217.4	146.4
243.15	87.6	120.7	181.3	220.2	247.7	213.5	143.6
238.15	86.7	119.2	178.5	216.6	243.5	209.4	140.8
233.15	85.6	117.6	175.6	212.8	239.0	205.3	138.0
228.15	84.4	115.9	172.6	208.9	234.5	201.0	135.1
223.15	83.2	114.0	169.5	204.8	229.8	196.7	132.1
218.15	81.9	112.1	166.2	200.7	224.9	192.2	129.0
213.15	80.4	110.1	162.8	196.4	220.0	187.7	126.0
208.15	79.0	108.0	159.3	192.0	215.0	183.1	122.8
203.15	77.4	105.8	155.8	187.5	209.9	178.5	119.7
198.15	75.8	103.6	152.1	182.9	204.7	173.8	116.5
193.15	74.1	101.3	148.4	178.2	199.4	169.0	113.2
188.15	72.4	98.9	144.6	173.5	194.1	164.2	110.0
183.15	70.7	96.5	140.7	168.7	188.6	159.3	106.7
178.15*	68.9	94.0	136.8	163.8	183.2	154.3	103.3
173.15	67.1	91.5	132.8	158.9	177.6	149.3	99.9
168.15	65.2	89.0	128.8	153.9	172.0	144.3	96.5

*Values given below this temperature were obtained by extrapolation.

Table 18. Derived Free Energy of Mixing of Ethanol-Methylcyclohexane System

x_a	0.0742	0.1979	0.3456	0.5324	0.8004
T°K.	Free Energy of Mixing cal./gm. mole				
308.15	-31.9	-56.8	-75.4	-91.6	-89.7
303.15	-29.7	-53.6	-71.7	-87.8	-86.7
298.15	-27.7	-50.6	-68.3	-84.1	-83.9
293.15	-25.9	-47.8	-65.0	-80.6	-81.1
288.15	-24.2	-45.2	-62.0	-77.3	-78.4
283.15	-22.7	-42.8	-59.1	-74.1	-75.8
278.15	-21.3	-40.6	-56.4	-71.1	-73.2
273.15	-20.1	-38.5	-53.8	-68.1	-70.7
268.15	-18.9	-36.5	-51.4	-65.3	-68.2
263.15	-17.9	-34.7	-49.1	-62.6	-65.8
258.15	-16.9	-32.9	-46.8	-59.9	-63.4
253.15	-16.0	-31.2	-44.7	-57.3	-61.0
248.15	-15.2	-29.6	-42.6	-54.7	-58.6
243.15	-14.4	-28.1	-40.6	-52.2	-56.3
238.15	-13.7	-26.7	-38.7	-49.7	-54.0
233.15	-13.1	-25.2	-36.8	-47.3	-51.6
228.15	-12.4	-23.8	-34.9	-44.9	-49.3
223.15	-11.8	-22.5	-33.0	-42.5	-46.9
218.15	-11.2	-21.1	-31.2	-40.1	-44.6
213.15	-10.7	-19.8	-29.4	-37.7	-42.2
208.15*	-10.1	-18.5	-27.6	-35.3	-39.9
203.15	-9.6	-17.3	-25.8	-32.9	-37.5
198.15	-9.1	-16.0	-24.1	-30.5	-35.1
193.15	-8.5	-14.7	-22.3	-28.1	-32.7
188.15	-8.0	-13.5	-20.6	-25.7	-30.2

*Values given below this temperature were obtained by extrapolation.

Table 19. Derived Free Energy of Mixing of Ethanol-Toluene System

x_a	0.0630	0.0969	0.1841	0.2748	0.4505	0.6439	0.8026
T°K.	Free Energy of Mixing cal./gm. mole						
308.15	-56.2	-69.7	-94.5	-113.1	-137.5	-147.8	-133.4
303.15	-53.1	-65.8	-89.5	-107.6	-131.8	-143.0	-129.7
298.15	-50.0	-62.0	-84.8	-102.5	-126.4	-138.3	-126.2
293.15	-47.1	-58.5	-80.4	-97.7	-121.4	-133.9	-122.9
288.15	-44.3	-55.1	-76.3	-93.2	-116.6	-129.8	-119.7
283.15	-41.7	-51.9	-72.4	-88.9	-112.1	-125.8	-116.7
278.15	-39.2	-48.9	-68.8	-35.0	-107.9	-122.1	-113.7
273.15	-36.9	-46.2	-65.4	-81.2	-103.9	-118.6	-110.9
268.15	-34.8	-43.6	-62.2	-77.8	-100.2	-115.3	-108.2
263.15	-32.7	-41.1	-59.2	-74.6	-96.7	-112.1	-105.7
258.15	-30.8	-38.9	-56.5	-71.6	-93.4	-109.1	-103.2
253.15	-29.1	-36.8	-54.0	-68.8	-90.3	-106.3	-100.8
248.15	-27.5	-34.8	-51.6	-66.2	-87.4	-103.6	-98.5
243.15	-26.0	-33.0	-49.4	-63.8	-84.7	-101.1	-96.3
238.15	-24.6	-31.3	-47.4	-61.6	-82.2	-98.6	-94.2
233.15	-23.3	-29.8	-45.6	-59.5	-79.8	-96.3	-92.1
228.15	-22.2	-28.3	-43.8	-57.6	-77.5	-94.1	-90.1
223.15	-21.1	-27.0	-42.2	-55.8	-75.4	-92.0	-88.1
218.15	-20.1	-25.8	-40.8	-54.1	-73.3	-89.9	-86.2
213.15	-19.1	-24.6	-39.4	-52.6	-71.4	-88.0	-84.4
208.15	-18.3	-23.5	-38.1	-51.1	-69.6	-86.1	-82.5
203.15	-17.5	-22.6	-36.9	-49.8	-67.9	-84.3	-80.8
198.15	-16.8	-21.6	-35.9	-48.5	-66.2	-82.5	-79.0
193.15	-16.1	-20.8	-34.8	-47.4	-64.7	-80.8	-77.3
188.15	-15.5	-20.0	-33.9	-46.3	-63.2	-79.2	-75.7
183.15	-14.9	-19.2	-33.0	-45.2	-61.8	-77.6	-74.1
178.15*	-14.3	-18.5	-32.2	-44.3	-60.4	-76.1	-72.5
173.15	-13.8	-17.9	-31.4	-43.3	-59.1	-74.6	-70.9
168.15	-13.3	-17.2	-30.7	-42.5	-57.9	-73.2	-69.4

*Values given below this temperature were obtained by extrapolation.

Table 20. Derived Activity Coefficients of Ethanol-Methylcyclohexane System

	Temperature °K.					
	308.15		273.15		248.15	
x_a	γ_a	γ_h	γ_a	γ_h	γ_a	γ_h
0.1	6.82	1.10	8.27	1.08	8.71	1.08
0.2	3.63	1.22	3.65	1.24	3.75	1.25
0.3	2.50	1.33	2.51	1.40	2.56	1.41
0.4	2.00	1.50	2.07	1.55	2.11	1.57
0.5	1.65	1.76	1.76	1.77	1.79	1.79
0.6	1.40	2.20	1.48	2.20	1.50	2.23
0.7	1.22	2.88	1.24	3.06	1.25	3.14
0.8	1.10	3.90	1.08	4.63	1.08	4.82
0.9	1.00	5.60	1.00	6.77	1.01	7.18

	223.15		198.15*	
x_a	γ_a	γ_h	γ_a	γ_h
1.0	9.11	1.08	9.57	1.08
2.0	3.87	1.25	4.04	1.25
3.0	2.63	1.42	2.72	1.42
4.0	2.15	1.58	2.22	1.59
5.0	1.83	1.81	1.87	1.83
6.0	1.52	2.27	1.55	2.30
7.0	1.26	3.21	1.28	3.28
8.0	1.09	5.01	1.10	5.22
9.0	1.01	7.67	1.01	8.32

*Values given at this temperature were obtained by extrapolation.

Table 21. Derived Activity Coefficients of Ethanol-Toluene System

	Temperature °K.					
	308.15		273.15		248.15	
x_a	γ_a	γ_h	γ_a	γ_h	γ_a	γ_h
0.1	5.33	1.04	6.40	1.06	6.88	1.07
0.2	3.12	1.14	3.25	1.19	3.27	1.21
0.3	2.27	1.27	2.26	1.34	2.25	1.37
0.4	1.80	1.44	1.81	1.51	1.82	1.53
0.5	1.50	1.67	1.53	1.73	1.55	1.75
0.6	1.29	2.01	1.32	2.08	1.32	2.12
0.7	1.15	2.49	1.15	2.63	1.15	2.74
0.8	1.06	3.15	1.05	3.53	1.04	3.70
0.9	1.01	4.10	1.00	4.54	1.00	4.69

	223.15		198.15		173.15*	
x_a	γ_a	γ_h	γ_a	γ_h	γ_a	γ_h
0.1	7.17	1.07	7.29	1.08	7.25	1.08
0.2	3.25	1.23	3.22	1.24	3.12	1.25
0.3	2.23	1.39	2.19	1.40	2.14	1.41
0.4	1.82	1.55	1.80	1.56	1.78	1.56
0.5	1.55	1.76	1.55	1.76	1.54	1.75
0.6	1.33	2.13	1.33	2.13	1.32	2.12
0.7	1.15	2.79	1.14	2.81	1.14	2.79
0.8	1.04	3.80	1.03	3.84	1.02	3.81
0.9	0.99	4.74	0.99	4.71	0.99	4.60

*Values given at this temperature were obtained by extrapolation.

APPENDIX F

CORRELATION OF THE ASSOCIATED THEORY OF SOLUTION WITH DERIVED EXCESS THERMODYNAMIC PROPERTIES

Method of Calculation

In order to obtain the values of the parameters b, K_{c2}, and K_{ci} that provided the best agreement between Equation (22) and the derived isothermal excess free energy data of the ethanol-methylcyclohexane system, the method of successive substitution was used[54]. The method is, briefly, as follows.

If a one variable equation

$$y = f(y) \tag{53}$$

satisfies the condition, $|\frac{df(y)}{dy}| < 1$, in a region near the root, y_o, the successive substitution

$$y_2 = f(y_1)$$
$$y_3 = f(y_2)$$
$$\cdots\cdots$$
$$y_n = f(y_{n-1})$$

will converge to the solution of Equation (53), i.e., y_n will approach y_o, provided that the starting value, y_1, is also in that region which satisfies the above condition.

For the two variable simultaneous equations,

$$y = f_1(y,z) \tag{54}$$
$$z = f_2(y,z)$$

The conditions for convergence are

$$\left|\frac{\partial f_1(y,z)}{\partial y}\right| + \left|\frac{\partial f_1(y,z)}{\partial z}\right| < 1$$

$$\left|\frac{\partial f_2(y,z)}{\partial y}\right| + \left|\frac{\partial f_2(y,z)}{\partial z}\right| < 1$$

and the successive substitution becomes

$$\begin{aligned}
y_2 &= f_1(y_1, z_1) \\
z_2 &= f_2(y_2, z_1) \\
y_3 &= f_1(y_2, z_2) \\
z_3 &= f_2(y_3, z_2) \\
&\cdots\cdots\cdots \\
&\cdots\cdots\cdots \\
y_n &= f_1(y_{n-1}, z_{n-1}) \\
z_n &= f_2(y_n, z_{n-1})
\end{aligned}$$

It was found that Equation (30) could be rearranged to the form

$$K_{ci}^2 C_1 = \frac{1}{2C_a}\left[K_{ci}^2 C_1^3 (K_{c2} - K_{ci}) - (2K_{ci} K_{c2} - 2K_{ci}^2 \right. \qquad (30A)$$

$$\left. - C_a K_{ci}^3) C_1^2 - K_{ci} C_1 + C_a K_{ci}\right] \cdots$$

When K_{c2}, K_{ci}, and C_a are known quantities, the value of C_1 can be obtained by successive substitution of the variable $K_{ci}^2 C_1$ into Equation (30A). Since Equation (30A) satisfies the condition of convergence as

given for Equation (53). The starting value of C_1 can be approximated by the following equation:

$$C_1 = (2K_{ci}^2 C_a) + K_{c2} - \frac{(4K_{c2} \cdot K_{ci}^2 C_a + K_{c2}^2)^{\frac{1}{2}}}{2 C_a K_{ci}^3} \cdots \qquad (55)$$

If one writes

$$B = \frac{1}{x_a}\left[\frac{G^E}{RT} - (x_h \ln \frac{C_h V_h}{x_h} - [(x_a V_a + x_h V_h) \cdot \sum_i C_i - x_a V_a \sum_i C_i^o]) - \frac{b}{RT} V^s D_a D_h\right]$$

Equation (22) can be rewritten in the following forms:

$$\frac{1}{K_{ci}} = C_a/K_{c2} C_1^o x_a e^B(1/(1 - C_1 K_{ci})^2 - 1 + K_{ci}/K_{c2}) \qquad (22A)$$

$$\frac{1}{K_{c2}} = [(1/(1 - C_1 K_{ci})^2) - 1] / K_{ci}[(C_a/(C_1^o x_a e^B)) - 1] \qquad (22B)$$

When the following quantities: temperature, molal volume of pure components, the parameter b, and G^E at x_a, are known, only two unknowns, K_{c2} and K_{ci}, remain in the Equations (22A) and (22B). If each equation is evaluated at a different x_a, Equations (22A) and (22B) become a set of independent simultaneous equations and can be used to solve for K_{c2} and K_{ci} using the method of successive substitution as illustrated for Equation (54). However, the excess free energy of the ethanol-methylcyclohexane system were derived at five different experimental compositions. In order that a single set of K_{c2} and K_{ci} be able to satisfy Equation (22) at all the five data points, Equations

(22A) and (22B) were successively evaluated at the five data points during the iteration. For a particular choice of b the iteration was carried out as follows:

1. The starting values for K_{c2} and K_{ci} were selected.

2. A derived G^E value and the corresponding x_a were selected.

3. C_1 and C_1^o were obtained from successive substitution of Equation (25A) using the above values.

4. $\sum C_i^o$ and $\sum C_i$ were obtained from Equation (31).

5. Substituting the above values into the right side of Equation (22A), a new value for K_{ci} was obtained.

6. The G^E calculated from Equation (22) using the current value of K_{c2} were compared with the derived G^E at all five compositions.

7. Steps (2), (3), and (4) were repeated using the current values.

8. Substituting the current values into the right side of Equation (22B), a new value for K_{c2} was obtained.

9. Step (6) was repeated.

10. Step (2) to Step (9) were repeated using the current values. When all the five data points, G^E vs. x_a, were selected once, the selection was repeated.

11. The iteration process was stopped when further iteration could not improve the agreement between the calculated G^E and the derived G^E. The final values of K_{c2} and K_{ci} were considered as the best values to represent the derived G^E.

The agreement between the calculated G^E and the derived G^E was judged by the magnitude of the sum of the absolute residual, SR,

which was defined as follows:

$$SR = \sum_{\substack{\text{all data} \\ \text{points}}} \left| 1 - \frac{G^E \text{calculated from Eq. (22)}}{G^E \text{ derived from } C_P^E \text{ data}} \right|$$

The above iteration has shown the following properties:

1. The deviations between the derived G^E and the G^E calculated using the final values of K_{c2} and K_{ci} were usually well distributed.

2. When the initial K_{c2} was selected to be larger than the final value, and the initial K_{ci} was selected to be smaller than the final value, the convergence of the iteration was very rapid showing a rapid decrease of SR. Near the final values of K_{c2} and K_{ci}, the values of K_{c2}, K_{ci} and SR would fluctuate in a narrow range during successive substitution, and then SR might diverge very slowly.

3. There existed different pairs of final values of K_{c2} and K_{ci} (depending on the choice of the starting values) which could fit the derived G^E equally well.

4. Even when Equation (22) could not possibly fit the derived G^E within the accuracy of the derived values, the above mentioned three properties were still found to be true. This property was very useful in the determination of the parameter b.

The determination of the parameter b and the different pairs of parameters K_{c2} and K_{ci} which could fit the derived G^E equally well are illustrated in the following sample calculation made at 273.15°K.

For purposes of convenience, the concentration unit used in the calculation was gram moles per 100 ml. The units of b and K_c were, therefore, cal./100 ml. and 100 ml./ gram mole, respectively.

A series of trial values: 200, 250, 300, 350, 400, and 450 were assigned to the parameter b. The range of trial values of b was selected in view of the b value obtained by Kretschmer and Wiebe[21]. For each value assigned to b, the method of successive substitution was used to search for the best fit between Equation (22) and the derived G^E by arbitrarily choosing the starting values of K_{c2} and K_{ci}. The property of the iteration method (property no. 2) mentioned before, provided some guide to the selection of starting values for K_{c2} and K_{ci}. With the starting value thus chosen, the successive substitution would converge to the best fit between Equation (22) and the derived excess free energy. Even different final K_c values are used, as shown in Table 22. The value of SR remains approximately the same for each value of b. A value of 0.1 in SR is equivalent to an average deviation of 2 per cent between the calculated G^E and the derived G^E. When SR is equal to 0.2 the average deviation (equivalent to 4 per cent) is much larger than the uncertainty in the derived G^E. This indicates that when b is larger than 350 or smaller than 200, Equation (22) cannot possibly be fitted to the derived G^E within the accuracy of the derived data. A plot of b vs. SR showed that the minimum value of SR lay in the region in which b was approximately 290; this value was used as the value of b at 273.15°K.

Table 22. Determination of the Parameter b at 273.15°K.

b cal./100ml.	Starting K_{c2} 100 ml./gm.mole	Starting K_{ci} 100 ml./gm.mole	Starting SR	Number of Substitutions	Final K_{c2} 100 ml./gm.mole	Final K_{ci} 100 ml./gm.mole	Final SR
200	50	110	0.37	19	25.8	177.4	0.14
250	50	100	0.24	24	31.9	150.8	0.073
250	60	125	0.19	21	41.7	166.3	0.074
300	60	120	0.070	5	54.1	122.0	0.067
300	40	70	0.219	12	27.6	95.4	0.073
350	40	70	0.109	4	31.0	70.2	0.106
350	50	100	0.117	3	50.4	97.6	0.116
400	50	80	0.204	4	44.9	72.4	0.198
400	40	70	0.200	3	39.8	66.7	0.196
450	50	75	0.350	12	55.3	68.6	0.309
450	30	55	0.340	9	27.0	50.3	0.312

After b had been determined, the different pairs of K_{c2} and K_{ci} which could fit the derived data equally satisfactorily were obtained by the method of successive substitution. Figure 6 shows the starting and the final values of K_{c2} and K_{ci} and also the path of the K_c values obtained from each substitution. The deviation, SR, between the G^E, calculated from the final values of K_c given in Figure 6, and the derived G^E are in the range of 0.06 to 0.075; mostly, the deviations are fairly well distributed. Therefore, the agreement between Equation (22) and the derived G^E does not provide a sufficient criterion to determine the values of K_{c2} and K_{ci}; but it does limit the

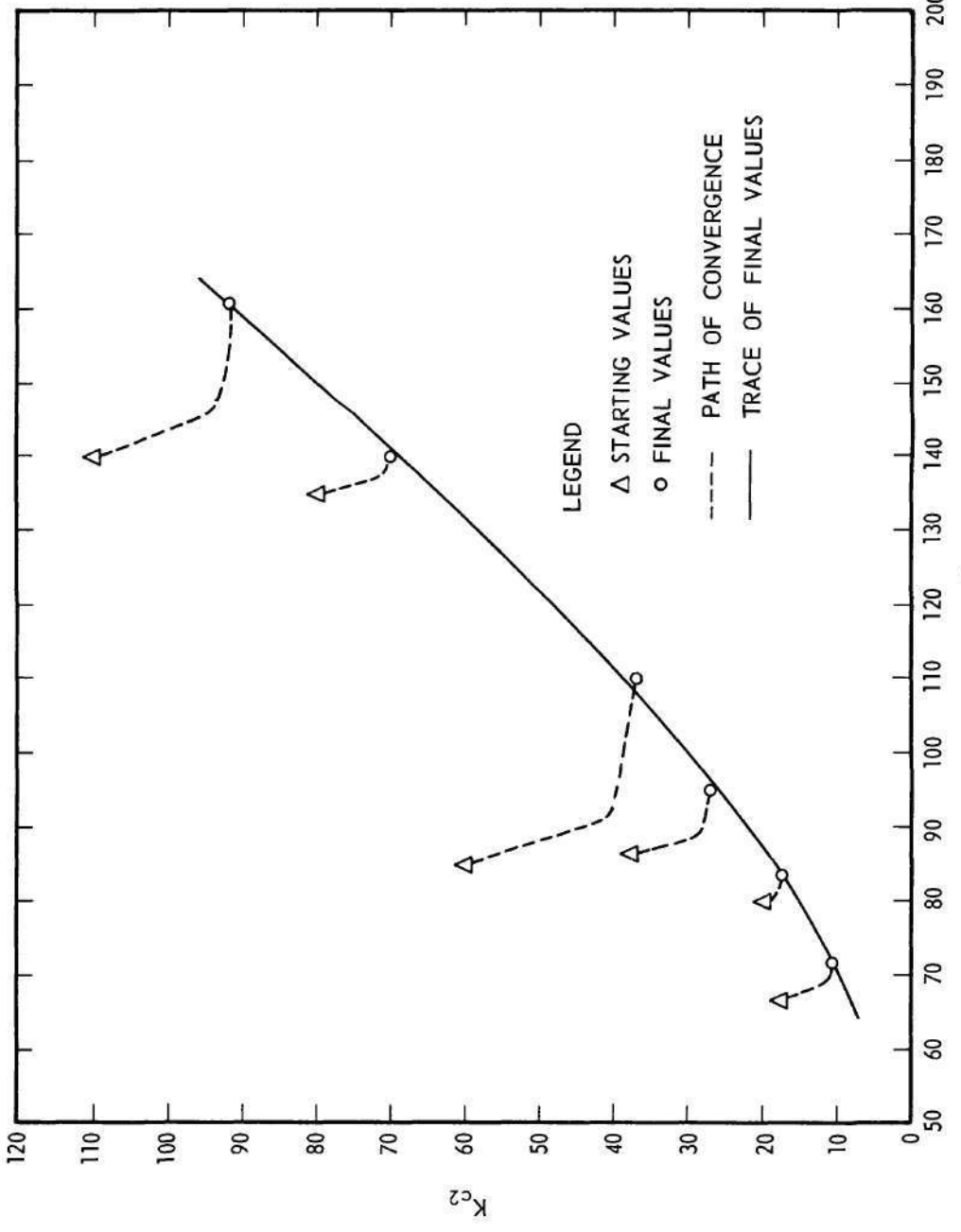

Figure 6. Determination of K_{c2} and K_{ci} at 273.15°K and b = 290 cal./100 ml.

values of K_{c2} and K_{ci} to a certain relation which is shown as a solid line in Figure 6.

If b, K_{c2} and K_{ci} are known, the H_2^R and H_i^R in Equation (41) can be obtained by fitting Equation (41) to the derived excess enthalpy using the least-squares method. When different pairs of K_{c2} and K_{ci}, taken from the solid line given in Figure 6, were used in Equation (41), it was found that the value of H_i^R was not very sensitive to the choice of K_c; while the value of H_2^R was very sensitive to different choices of K_c, as shown in Table 23.

Table 23. Determination of H_2^R and H_i^R at 273.15°K. and b = 290 cal./100 ml.

K_{c2} 100 ml./gm.mole	K_{ci} 100 ml./gm.mole	H_2^R cal./gm.mole	H_i^R cal./gm.mole
8	65	-6692	-1960
12	75	-1992	-1779
17	83	+869	-1606
30	100	+3611	-1357
40	110	+4395	-1254
60	130	+5124	-1176

The value of H_2^R was expected to be reasonably close to the value of H_i^R. Therefore, $K_{c2} = 12$ and $K_{ci} = 75$ were chosen as the correct values at this temperature. The values of H_2^R and H_i^R were adjusted slightly, so that $H_i^R = H_2^R$ and Equation (41) still agreed with the

derived H^E. The final value for H_i^R thus obtained was -1777 cal./gm. mole. Therefore, at 273.15°K., the four parameters b, K_{c2}, K_{ci}, and H_i^R were determined to be 290, 12, 75, and -1777, respectively. The other parameter, H_2^R, was arbitrarily chosen to be equal to H_i^R.

The above proceudres were used to determine all of the parameters at 308.15°K., 273.15°K., and 248.15°K., and the parameter b at 223.15°K. and 198.15°K. The values of H_i^R obtained at the three higher temperatures were extrapolated graphically to 223 and 198 K. The equilibrium constant, K_i, at these two lower temperatures were estimated by Equation (44), using the K_i determined at 248.15°K. and the extrapolated H_i^R. After K_i at these two lower temperatures were obtained, K_2 or K_{c2} were obtained from the relations between K_{c2} and K_{ci}, given as the solid line in Figure 6, determined at these two temperatures from the correlation of excess free energy data with Equation (22). The parameters determined according to the method described above are listed in Table 24. The comparison between the calculated G^E and H^E, computed from Equations (22) and (41) and the given parameters, and the derived G^E and H^E are tabulated also in Table 24. These parameters, after conversion to the more commonly used concentration units of gm.mole/liter are given in Table 4, Chapter VI.

Table 24. Comparison of the Derived and the Calculated G^E and H^E

Temp. 308.15°K.

b = 280 cal./100 ml. H_i^R = 3590 cal./gm.mole

K_{c2} = 6.5 100 ml./gm.mole K_{ci} = 44 100 ml./gm.mole

	G^E cal./gm.mole		H^E cal./gm.mole	
x_a	Derived*	Calculated**	Derived*	Calculated***
0.0742	130.0	126.1	108.2	111.1
0.1979	247.7	249.0	149.4	148.1
0.3456	319.3	322.4	160.2	163.4
0.5324	331.4	334.9	153.2	150.1
0.8004	216.3	212.6	95.4	92.1

Temp. 273.15°K.

b = 290 cal./100 ml. H_i^R = 1777 cal./gm.mole

K_{c2} = 12 100 ml./gm.mole K_{ci} = 75 100 ml./gm.mole

	G^E cal./gm.mole		H^E cal./gm.mole	
x_a	Derived*	Calculated*	Derived	Calculated
0.0742	123.4	120.0	45.4	46.4
0.1969	231.5	232.0	72.5	70.3
0.3456	296.0	298.4	82.6	85.3
0.5324	306.9	309.3	89.1	90.3
0.8004	200.5	196.4	65.3	62.8

(Continued next page)

*These derived values are taken from Table 16, Appendix E.

**The G^E are calculated from Equation (22) using the given parameters.

***The H^E are calculated from Equation (41) using the given parameters.

Temp. 248.15°K.

b = 295 cal./100 ml. H_i^R = 942 cal./gm.mole

K_{c2} = 20 100 ml./gm.mole K_{ci} = 105 100 ml./gm.mole

x_a	G^E cal./gm.mole		H^E cal./gm.mole	
	Derived	Calculated*	Derived	Calculated
0.0742	115.1	112.5	24.0	26.6
0.1979	215.6	215.9	47.6	46.9
0.3456	275.2	277.4	58.3	63.0
0.5324	286.0	287.7	70.7	71.9
0.8004	187.7	183.2	58.1	53.4

Temp. 223.15°K.

b = 310 cal./100 ml. H_i^R = 650 cal./gm.mole

K_{c2} = 26 100 ml./gm.mole K_{ci} = 120 100 ml./gm.mole

x_a	G^E cal./gm.mole		H^E cal./gm.mole	
	Derived	Calculated	Derived	Calculated
0.0742	105.4	103.3	14.7	21.4
0.1979	198.0	198.5	37.4	41.2
0.3456	252.8	255.8	48.7	58.1
0.5324	263.9	266.3	64.7	68.2
0.8004	174.6	170.7	57.5	52.1

Temp. 198.15°K.

b = 320 cal./100 ml. H_i^R = 500 cal./gm.mole

K_{c2} = 33 100 ml./gm.mole K_{ci} = 135 100 ml./gm.mole

x_a	G^E cal./gm.mole		H^E cal./gm.mole	
	Derived	Calculated	Derived	Calculated
0.0742	95.0	93.6	11.3	18.7
0.1979	179.8	180.2	34.3	38.2
0.3456	229.7	233.0	45.2	55.2
0.5324	241.5	143.7	63.9	66.1
0.8004	161.6	157.3	60.1	51.1

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He moved to Taipei, Taiwan, in 1948 and was graduated from Chien Kuo High School in 1951. From 1951 to 1955, he attended the National Taiwan University and was awarded the degree of Bachelor of Chemical Engineering. He was commissioned Second Lieutenant in the Army of the Republic of China in 1955, and served in the Liaison Bureau of the Ministry of Defense until his release from active duty in 1957.

He came to the United States in 1957 to enroll in the Graduate Division of the Georgia Institute of Technology through the sponsorship of the Rotary Club of Atlanta, Georgia. He was employed as research assistant in the School of Chemical Engineering from 1958 to 1959. He received the degree of Master of Science in Chemical Engineering in June, 1959. His M. S. thesis, entitled Phase Equilibria in Nitroparaffin-Hydrocarbon Systems, was done under the supervision of Dr. W. T. Ziegler. He was employed as a graduate assistant in the School of Chemical Engineering from 1959 to 1960 and was then employed as research assistant in the Engineering Experiment Station until June, 1963. During the period from 1960 to 1962, he also served occasionally as teaching assistant in the evening division, School of Mathematics.

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